4

The PVC Formulations

The formulations are presented in alphabetical order of the method of processing used to manufacture a particular product. Any production method may have several products listed under the production method category, and for these products, formulations are presented in a breakdown for formulations proposed by the raw material suppliers, found in the open literature, or patents (if the information in any of these groups is available). Usually, the most recent formulations are presented, considering that always changing requirements affect formulation and make some formulations and methods of production obsolete. In some cases, older data are given, either to highlight the composition of products which may be reused by recycling or because newer formulations were not available or because the formulation has educational value today.

4.1 BLOW MOLDING

Blow molding is the primary method of production of hollow plastic objects. It can be performed by:

- extrusion blow molding
- injection blow molding
- stretch blow molding

Extrusion blow molding is usually used for the production of bigger articles (weight of 360 g and more) unlike in the case of injection blow molding where small articles, having a well-controlled wall thickness, are produced. In both methods, the first step is that of production of a parison which is a preform to be inflated in the next step against internal mold walls. Stretch blow molding is most frequently used for crystalline polymers (e.g., PET) but biaxial stretching (orientation) can also be used in the case of PVC bottles to improve their mechanical properties (see Section 4.1.1). Many polymers are used as raw materials in blow molding processes. PVC has several important features such as high clarity, excellent acid resistance, good barrier properties to oxygen, and good oil resistance. This makes it useful for many applications. The usual drawbacks of PVC are low distortion temperature, inferior impact resistance (which can be improved by impact modification), poor heat resistance (which can be improved by proper selection of stabilizers), and average cold resistance.

4.1.1 BOTTLES AND CONTAINERS

Bottles and containers are the major products of blow molding. The major novelties in this technology are probably due to the application of multilayered products to improve mechanical performance, barrier properties, and weathering resistance. These are products of different polymer layers, and as such, they are not discussed here.

4.1.1.1 Formulations proposed by the raw material suppliers

Bottles. [Data from **Mark 1984E**. Technical data sheets. *Crompton*. March 2003.]

Raw material	Concentration, parts
PVC (low to medium molecular weight)	100
FDA-cleared impact modifier	5-15
Acrylic process aid	2.5
Internal/external lubricant	1-1.5
Mark 1984E (methyltin mercaptide)	1.5-2

Clear bottle, food packaging. [Data from **Advastab TM-2080**. *Rohm & Haas*.]

Raw material	Concentration, parts
PVC (K=58)	100
Paraloid K-120N (process aid)	1
Paraloid BTA-733 (impact modifier)	15
Advalube F-1005 (internal lubricant)	0.25
Advalube E-2100 (external lubricant)	0.5
Advastab TM-2080 (thermal stabilizer)	1.5

Thermal stabilizer used in this formulation was intentionally developed for the process. It gives excellent thermal stability (stability time of 26.4 min compared with 17.2 min for octyltin mercaptide/maleate which are commonly used for such applications).

Food-grade bottle. [Data from **Thermolite 890**. *Arkema*.]

Raw material	Concentration, parts
PVC (K=57)	100
Thermolite 890	1.5-2
Internal lubricant	1.5-2
External lubricant	0.1-0.2

Food-grade bottle. [Data from **Thermolite 890**. *Arkema*.]

Raw material	Concentration, parts
Plastistrength 550	1.5-2
Plastistrength 710	0.5-1
Clearstrength 320	12-15
Toner	quantum satis

4.1.1.2 Formulations found in the open literature

One reference regarding extrusion blow-molding formulation includes PVC having K=57 and about 11.5 wt% of additives, such as a tin stabilizer, impact modifier, process aids, lubricants, and a small amount of pigment (Glomsaker, T.; Hinrichsen, E. L.; Thorsteinsen, P., *Polym. Eng. Sci*., **41**, 12, 2231-2248, 2001.).

Clear bottles/sheet. [Data from Carroll, W. F., Johnson, R. W., Moore, S. S., Paradis, R. A., **Applied Plastics Engineering Handbook**, Chapter 5. Poly(vinyl chloride), *Elsevier*, 2011, p. 61-76.]

Raw material	Concentration, parts
PVC	100
Stabilizer	high tin
Impact modifier	6-10
Processing aid	0.5-2
Oxidized PE	0.-0.3
Pigments	q.s.

4.1.1.3 Patented inventions

Bottle compound for extrusion blow-molding process. [Data from King, L. F.; Taylor W., **US Patent 3,666,700**, May 30, 1972.]

Raw material	Concentration, parts
PVC (K=63)	100
Thio-organotin stabilizer	2
Diisodecyl phenyl phosphite	1.5
White oil	0.5
Polymethylmethacrylate process aid	3
Methacrylate-butadiene-styrene impact modifier	12
Microcrystalline wax	0.5

In another development, PVC bottles of thin-wall construction were produced by biaxial stretching of the preform by rapid blow molding to the mold's dimensions. The stretch rates were between 100 and 1000%. The best result was obtained when stretching was 225% and stretch time 3 seconds (Hafner, W.; Hufnagel, W, **US Patent 3,980,192**, Sept. 14, 1976.)

Clear, odorless bottles. [Data from Wypart, R. W.; Summers, J. W., **US Patent 4,751,118**, Jun. 14, 1988.]

Raw material	Concentration, parts
Mass PVC	100
Impact modifier	10
Lubricants and process aids	2
Calcium stearate	0.1
Zinc stearate	0.2
β-diketone mixture costabilizer	0.2
Epoxidized soybean oil	5
Triglycerol monostearate	1
Polymeric phosphite	0.8

Cosmetic container having nacreous gloss. [Data from Odate, R.; Haga, T., **US Patent 4,847,323**, Jul. 11, 1989.]

Raw material	Concentration, parts
PVC (polymerization degree=1100)	100
Impact resistant polystyrene	20
Impact modifier (MBS)	15
Stabilizer (tin laurate)	1
Stabilizer (tin maleate)	2
Lubricant (stearyl alcohol)	1
Lubricant (stearic acid)	0.5

Bottle compound with improved process stability. [Data from Balasko, M.; Skillicorn, D. E.; Forsyth, T. H., **CDN Patent 2,053,019**, Apr. 20, 1992.]

Raw material	Concentration, parts
PVC	100
Disodium hydrogen phosphate	5
Impact modifier	13.5
Process aid	3
Organotin stabilizer	2
Calcium carbonate	5
Lubricants	4

Bottle compound with improved optical properties due to application of lubricant package. [Data from Fahey, T. E.; Falter, J. A; Hall, L. K., **US Patent 5,077,331**, Dec. 31, 1991.]

Raw material	Ca/Zn	Sn
	Concentration, parts	
Mass PVC (M_n=25,000-35,000)	100	100
Octyltin mercaptide stabilizer	2	
Acrylic process aid	2	2
Acrylic impact modifier	12	10
Blue toner	0.05	0.05
Ca/Zn stabilizer		0.5-1
Epoxidized soybean oil		5
Phosphite chelator		1
External lubricant	0.2-1	0.2-1
Internal lubricant	1-2	1-2

Frosted bottles. [Data from Cozens, R. J.; Greenlee W. S.; Skillicorn, D. E., **US Patent 5,247,019**, Sep. 21, 1993.]

Raw material	Concentration, parts
PVC	80
Crosslinked PVC	20
Tin stabilizer	2

Frosted bottles. [Data from Cozens, R. J.; Greenlee W. S.; Skillicorn, D. E., **US Patent 5,247,019**, Sep. 21, 1993.]

Raw material	Concentration, parts
Impact modifier	10.5
Process aid and lubricants	2.95
Blue tint	0.4

Glass bottles are made frosted by etching the glass surface to enhance light scattering. In the case of polymeric bottles, a frosted look can be achieved by sandblasting of the mold, but it is expensive. The formulation included in the above table can be used for both extrusion and injection blow molding processes. The frosting effect is achieved because polymers used in the composition have different viscoelastic properties and refractive indices. The degree of crosslinking affects the composition. The more crosslinked the polymer, the lower the concentration required.

4.1.2 OTHER PRODUCTS

4.1.2.1 Formulation proposed by the raw material supplier

Ca/Zn shrink-wrap film, blown film extrusion. [Data from **Waxes for PVC Lubrication**. *Clariant*, 2013.]

Raw material	Concentration, parts
S-PVC (K=60)	100
Ca/Zn stabilizer	2
Phthalate plasticizer	8-11
Epoxidized soybean oil	2.5
PMMA processing aid	1
Impact modifier	6
Glycerol monostearate	0.2
Licowax OP	0.3

4.1.2.2 Formulation found in the open literature

Starting formulation for injection blow molding. [Data from Stevenson, J. C.; Fazey, A. C., *J. Vinyl Additive Technol.*, **3**, 2, 118-125, 1997.]

Raw material	Concentration, parts
PVC (K=50-55)	100
Tin stabilizer	2
Internal lubricant (glycerol monostearate)	2.7
External lubricant (polyethylene wax)	0.3

Starting formulation for injection blow molding. [Data from Stevenson, J. C.; Fazey, A. C., *J. Vinyl Additive Technol*., **3**, 2, 118-125, 1997.]

Raw material	Concentration, parts
Acrylic process aid	1-2
Lubricating acrylic process aid	1-1.5
Impact modifier	10-12
Titanium dioxide and other colorants	1-2 (interior), 10-12 (exterior use)

4.1.2.3 Patented inventions

Corrugated pipe for dusts, hoses, and boots. [Data from Yamato, S. T.; Sagamihara, M. H.; Yamato, Y. I., **US Patent 4,424,834**, Jan. 10, 1984.]

Raw material	Concentration, parts
PVC (polymerization degree=2500)	100
Plasticizer (adipic acid propylene glycol, MW=1000)	70
Talc	20
Epoxidized soybean oil	3
Heat stabilizer (Ca/Zn)	2

Elastic PVC articles are inferior in comparison to vulcanized rubbers used for the production of corrugated pipe articles regarding their tensile and tear strengths, and deterioration of their flexibility with a time of use. This was improved by multilayer material. Three layered material gave the best performance. The outer layer was made out of polyester elastomer (Pelprene P-70B), the inner layer from polyester elastomer (Hytrel HTG-4275), and the intermediate layer from PVC having formulation given in the above table.

Pipe liner composition. [Data from Gargiulo, J. L., **WO Patent 1994/028344**.]

Raw material	Concentration, parts
PVC (Formolon 622)	100
Stabilizer (Advastab TM 694)	1.313
Internal lubricant (calcium stearate)	0.413
External lubricant (Wax 355 Hoechst Cellanese)	1.25
Process aid (Paraloid K-175)	1
Process aid (Paraloid K-120 N)	2.78
Plasticizer (Elvaloy 742P)	26
UV stabilizer (titanium dioxide)	5

This particular pipe is useful in repair (relining) of sewage system without the necessity of dismantling but by blow molding new liner inside the original pipe.

Heat-insulating, transparent PVC sheet. [Data from Shich, S-Y, Fung, D-R, Huang, Y-T, Lin, C-H, Cheng, C-H, Wu, W-Y, **US Patent 8,257,632**, Sep. 4, 2012, *Nan Ya Plastics Corporation*, Taiwan.]

Raw material	Concentration, parts
PVC	100
DINP	40
CeB_6	0.25
Ba-Zn thermal stabilizer	3
Stearic acid	0.4
Coupling agent	0.81
Dispersant	0.17
UV absorber	0.8

A small amount of either LaB_6 or CeB_6 alone as inorganic heat-insulating particles or in combination with a small amount of ATO as inorganic heat-insulating particles was uniformly dispersed in a PVC mixture. The 0.2 mm sheet produced from the above formulation has a light transmittance of 69%, a haze of 2.6%, the infrared cutting-off rate of 91% and UV cutting-off rate of 99%.

Blow molding composition of high flowability and excellent mechanical strength. [Data from Nagata, S.; Sodeyama, O., **US Patent 5,424,363**, Jun. 13, 1995.]

Raw material	Concentration, parts
PVC (polymerization degree=700)	100
Acrylic graft copolymer	7
EVA resin	3
AS resin (Cevian FD)	7
Tin stabilizer	1
Calcium stearate	0.7
Calcium carbonate	6
Polyethylene wax	0.5

Polymer blend with recycled poly(vinyl butyral). [Data from Hofmann, G. H., **US Patent** 6,506,835, Jan. 14, 2003.]

Raw material	Concentration, parts
PVC	100
PVB	50
EVA	20
Antioxidant	1

Large quantities of poly(vinyl butyral) can be recovered from car windshields where it has been used as an intermediate layer between two panes of glass. This recovered polymer can be reused for useful articles produced by blow molding using blending techniques described in the invention.

Vinyl foam containing acrylic process aid. [Data from Lavallee, P. R., **World Patent WO2011041195**, Apr. 7, 2011, *Arkema Inc*.]

Raw material	Composition, parts
PVC (K 57)	100
Thermolite 161 (tin stabilizer)	2.5
Calcium stearate	0.70
Paraffin wax	1.0
Oxidized polyethylene wax	0.2
High molecular process aid of invention	7.5
Plastistrength 770 (low molecular weight process aid)	2.0
Filler	5.0
Pigment	4.0

The new process aid is an acrylic copolymer containing 50 to 79 wt% methyl methacrylate. Incorporation of this process aid increased fusing rate and decreased temperature.

Stabilization of halogenated polymers. [Data from Cho, J-Y, Lundquist, E G, **World Patent WO2013085714**, Jun. 13, 2013, *Rohm and Haas*.]

Raw material	Concentration, parts
PVC or CPVC (e.g., TempRite 677 X670)	100
Paraloid KM-X100Pro (impact modifier)	5.5
Titanium dioxide	4.4
Calcium carbonate (Omyacarb UF-FL)	2.27
Advalube E-2100 (ester lubricant)	1.1
AC-629A (oxidized polyethylene	0.55
AC-316A (oxidized polyethylene)	0.55
AC-617A (polyethylene)	0.83
Irganox 245 (phenolic antioxidant)	0.15
Methyl tin mercaptide	0.2-2
Polymeric polyacid salt (Acumer 101)	0.2-2

Poly(vinyl chloride) or a chlorinated polyvinyl chloride is stabilized with a composition comprising either methyl, butyl or octyl tin mercaptide stabilizer and salt of a polymeric polyacid material in the solid form. The last improves the performance of tin stabilizer, especially if the moisture level in the composition is higher than 0.52 wt%.

Blow-molded metallized hot shrinkable film [Data from **CN105602144A**, May 25, 2016.]

Raw material	Concentration, parts
PVC	100
Organotin stabilizer	2.1
Plasticizer	5
Toughening agent MBS	5
Processing aid ACR	3.8
Internal lubricant	1.2
External, lubricant	0.9
Silver powder pigment	1.5

4.1.3 CONCLUSIVE REMARKS

Typical blow molding formulation includes the following components:

- PVC (low to medium molecular weight)
- impact modifier (usually acrylic and at relatively high concentration)
- acrylic process aid
- internal lubricant
- external lubricant
- thermal stabilizer (usually mercaptotin, the most classical, a combination of octyltin mercaptide with octyltin maleate; zinc stabilizers in combination with phosphites, epoxidized soybean oil, polymeric antiacid, and diketones are also applicable)

The above general formulations show that in material development, the most important properties are:

- impact strength (bottles and various containers are the major products, and they require good impact strength)
- the balance of good impact strength and flow properties (for good flow properties lower molecular weight PVC is used therefore its impact properties must be improved by impact modifiers; good flow is enhanced by selection of process aids, and internal and external lubricants and their proportions)
- thermal stability (material is exposed to two thermal processes: formation of parison and formation of the final product. For this reason, two groups of raw materials are essential: rheological additives (lubricants and process aids) and thermal stabilizers. The first group reduces the damage of polymer by reducing shear strength; the second group should effectively reduce the catalytic influence of HCl. Tin stabilizers are known for their stabilizing efficiency, and they offer long term stability without the catalytic impact of their reaction products. For this reason, they are frequently selected for this processing method.)

Many problems in the manufacturing of final products by blow molding are controlled by proper selection of parameters under which machinery is operated (not a subject of this book), but some can also be remediated by formulation change, for example:

- parison blow out (too low melt strength, too high melt temperature, resin swell characteristics)
- polymer sticking to core rods (inadequate lubrication)
- polymer sticking to parison mold (inadequate lubrication)
- inconsistent tail length (regrind variability)
- product wall thickness variability (use material having lower melt index)
- fisheyes or bubbles (high resin moisture or resin quality or contamination)
- black streaks or specs (excessive thermal degradation or material contamination)

- color change (excessive thermal degradation)
- warpage (melt strength)
- changes in color, strength, or appearance (percentage or quality of regrind)
- low production output (problems with lubricant selection)

Further reading, especially in the area of equipment control:
Lee, N., *Practical Guide to Blow Moulding*, **Rapra**, 2006.

4.2 CALENDERING

4.2.1 FILM

4.2.1.1 Formulations proposed by the raw material suppliers

Ca/Zn shrink-wrap formulation. [Data from **Waxes for PVC Lubrication**. *Clariant*, 2013.]

Raw material	Concentration, parts
PVC (K=60)	100
Ca/Zn stabilizer	2
Phthalate plasticizer	8-11
Epoxidized soybean oil	2.5
PMMA processing aid	1
Impact modifier	6
Glycerol monostearate	0.2
Licowax OP/Licolub WM 31/Licocare SBW 11 TP	0.2

Ca/Zn blood bag formulation. [Data from **Waxes for PVC Lubrication**. *Clariant*, 2013.]

Raw material	Concentration, parts
S-PVC (K=70)	>50
calcium stearate + zinc stearate	1
Plasticizer (DOP)	<40
Epoxidized soybean oil	<10
Licowax C/Licolub FA1 vegetable based	1

Sulfide-resistant calendered film. [Data from **Mark RFD**. Technical data sheet. *Crompton*.]

Raw material	Concentration, parts
PVC (medium to high molecular weight)	100
Phthalate plasticizer	40
Calcium carbonate	0-20
Drapex 4.4	5-10
Mark RFD (liquid Ba/Zn stabilizer)	3
Stearic acid	0.25

S-PVC calendering formulation. [Data from **Paraloid BTA-780S MBS impact modifier for PVC packaging applications**. *DowDuPont* 874-01721-0810.]

Raw material	Concentration, parts
S-PVC K57	100
Paraloid K-125	0.5
Paraloid K-175	1.0
Tin mercaptide stabilizer	1.3
Glycerol monooleate	0.5
Ester of montanic acid partially saponified with Ca	0.2
Toner OB 8	0.02
Toner 20	0.01

S-PVC calendering formulation stabilized with calcium/zinc stabilizer.

[Data from **Paraloid BTA-780S MBS impact modifier for PVC packaging applications**. *DowDuPont* 874-01721-0810.]

Raw material	Concentration, parts
S-PVC K57	100
MBS modifier	8.0
Paraloid K-175	0.2
Calcium behenate	0.3
Zinc octoate	0.08
Epoxidized soybean oil	5.5
Stearoyl benzoyl methane	0.125
DHP 507	0.0
Hydrogenated castor oil	1.25
Ester of montanic acid partially saponified	0.4
Polar polyethylene wax (oxidized)	0.2
Blue toner	0.2

Use of Elvaloy for plasticization [Data from Formulating for Improved PVC Performance with Elvaloy®, DuPont, 2014.]

Raw material	Concentration, parts
PVC	100
Elvaloy 741	50-100
Epoxidized soybean oil	3
$CaCO_3$	20
Mark 329	0.5
Stearic acid	3
$MgCO_3$	0.5
Therm-Check 1238	3
Irganox 101	1

PVC compounds plasticized with Elvaloy® HP may be calendered, extruded, or injection molded. Calendering compounds containing Elvaloy® HP requires more effective lubricants than the compounds with liquid plasticizers. For a thick flexible film, a temperature profile across the calender of 149-174°C (300-345°F) is usually suggested. In extrusion, melt temperatures should reach 182-193°C (360-380°F).

Non-sulfide staining film. [Data from *Pautai Industrial Corporation*, Taiwan.]

Raw material	Concentration, parts
PVC	100
DOP	35-60
ESBO	2-3
BZ-591	1.5-2.5
BZ-424	0-0.4

4.2.1.2 Patented inventions

Film having low VOC emission (less than 1,000 μg/m^2/h). [Data from Sobieski, R. T., **US Patent 7,029,759**, Apr. 18, 2006.]

Raw material	Concentration, parts
PVC	97.5
Acrylic resin	2.5
Calcium carbonate	47

Film having low VOC emission (less than 1,000 μg/m²/h). [Data from Sobieski, R. T., **US Patent 7,029,759**, Apr. 18, 2006.]

Raw material	Concentration, parts
Aluminum hydrate	3
Ca/Zn stearate	0.25
Stearic acid	0.3
Zn stearate	0.2
Diisononyl phthalate	40.5
Antifungal, antimicrobial	0.75
Epoxidized soybean oil	3
Organic phosphite+diluent (alcohol C12+)	2.2
Antimony oxide	4

Antistatic, transparent film. [Data from Milan, S., **US Patent 6,835,765**, Dec. 28, 2004.]

Raw material	Concentration, parts
PVC (K=70)	100
DOP	50
Epoxidized soybean oil	2
Ca/Zn stabilizer	2
Triethanolamine distearate	0.9
Pentaerythritol	0.1

Film with dimensional stability. [Data from Schramer, K. M.; Ocampo D. O., **US Patent 4,223,054**, Sep. 16, 1980.]

Raw material	Concentration, wt%
PVC (medium molecular weight)	25.1
PVC (high molecular weight)	25.1
Acrylic polymer resin	5
Di-(2-ethylhexyl) phthalate	5
Diisodecyl phthalate	5
Epoxidized soybean oil	4
Ba/Cd stabilizer (obsolete)	3
Colloidal silica	1
UV absorber	1
Titanium dioxide	25

Transparent film without facial flow marks and pits. [Data from Lin, T.-H., **US Patent 6,649,105**, Nov. 18, 2003.]

Raw material	Concentration, parts
PVC (polymerization degree=1250)	100
Dioctyl phthalate	40
Ba/Zn stabilizer	2-4

The elimination of facial flow marks and pits is accomplished by manufacturing technology rather than formulation. In the invented method, a film from the calender directly enters a water bath tank which partially cools material and crystallizes it. The material then passes a set of pressing rollers which preferably include 3 sets of rubber/metal rollers.

High gloss film. [Data from Pfaendner, R.; Malzacher, K., **US Patent 6,569,926**, May 27, 2003.]

Raw material	Concentration, parts
PVC (K=65-68, Norvinyl S 6775)	100
Chalk (Omyalite 95T)	2
Gloss improving compound (2-imidazolidone)	0.1
Gloss improving compound (Araladite GY 250)	2
Calcium stearate	0.8
6-amino-1,3-dimethyl-uracil	0.2
Alkamizer I	1
Maltilol	0.4
Irgawax 367	0.7
PE wax 520	0.5
AC 629 A (Allied Chemicals)	0.2

Film (new method of stabilization). [Data from Friedrich, H.-H.; Kuhn, K.-J.; Wehner, W.; Hopfmann, T., **US Patent 7,393,887**, Jul. 1, 2008.]

Raw material	Concentration, parts
PVC (K=70)	100
Dioctyl phthalate	44
Epoxidized soybean oil	6

Film (new method of stabilization). [Data from Friedrich, H.-H.; Kuhn, K.-J.; Wehner, W.; Hopfmann, T., **US Patent 7,393,887**, Jul. 1, 2008.]

Raw material	Concentration, parts
Aryl alkyl phosphite (Mark CH 300)	0.26
Alkyl nonylphenol phosphite (Mark CH 302)	0.26
Sodium perchlorate	0.04
Ester lubricant (Loxiol G 71 S)	0.3
Calcium stearate	0.2
Triethanolamine	0.5

Combination of perchlorate and amine contributes to improved stability of many PVC compositions including the above formulation. Addition of phosphite and epoxidized soybean oil further stabilize PVC. The alternative stabilizing formulations are given in the tables below.

Film (a new method of stabilization). [Data from Hopfmann, T.; Friedrich, H.-H.; Kuhn, K.-J.; Wehner, W., **US Patent 7,358,28**6, Apr. 15, 2008.]

Raw material	Concentration, parts
PVC (K=70)	100
Di-(2-ethylhexyl) phthalate	47
Epoxidized soybean oil	3
Ester lubricant (Loxiol G 71 S)	0.3
Calcium stearate	0.1
30% solution of sodium perchlorate in butyl diglycol	0.5
1,3-dioctyl-4-aminouracil	0.2
Diethanolsoyamine	0.2

Film (a new stabilizing formulation). [Data from Krainer, E.; Bacaloglu, R.; Shah, M.; Fisch, M. H.; Frenkel, P.; Bae, K. J., **US Patent 7,282,527**, Oct. 16, 2007.]

Raw material	Concentration, parts
PVC (Oxy 450)	100
Diisooctyl phthalate	45
Epoxidized soybean oil	5
Calcium stearate	0.5
Organic phosphite	1
Antioxidant	0.3

Film (a new stabilizing formulation). [Data from Krainer, E.; Bacaloglu, R.; Shah, M.; Fisch, M. H.; Frenkel, P.; Bae, K. J., **US Patent 7,282,527**, Oct. 16, 2007.]

Raw material	Concentration, parts
Polyethylene glycol 200	0.35
6-amino-1,3-dimethyluracil	0.6
60% solution of sodium perchlorate	0.25

Film stabilized with phosphite to reduce concentration of metal stabilizer. [Data from Stevenson, D. R.; Jennings, T. C.; Harr, M. E.; Jakupca, M. R., **US Patent 7,320,764**, Jan. 22, 2008.]

Raw material	Concentration, parts
PVC	100
Plasticizer	38
Epoxidized soybean oil	3
Stearic acid	0.2
Zinc stearate	0.08
Phosphite (Doverphos 479)	1

Liquid thermal stabilizer having no toxicological impact. [Data from Romagnano, S, Li, B G, **World Patent WO2010000734**, Jan. 7, 2010, *Lamberti Spa*.]

Raw material	Concentration, parts
PVC-S K70	100
DIDP	32
Epoxidized soybean oil	3
$CaCO_3$	20
TiO_2	15
Barium-zinc salts (3.5 to 4:1 ratio)	2.5
Organic phosphite	0.1-0.35

Film with more efficient plasticizer. [Data from Goss, C.; Larson, M.; Legrand, P. J. P.; Caers, R. F.; Daniels, P. H.; Godwin, A. D.; Naert, D., **US Patent 7,413,813**, Aug. 19, 2008.]

Raw material	Concentration, parts
PVC (Solvic 271 GC)	100
Di-(2-ethylhexyl) cyclohexanoic acid ester	35
Ba/Zn stabilizer (Lankromark LZB 732)	2
Epoxidized soybean oil	0.5

Use of esters of cyclohexanone polycarboxylic acids, such as di-(2-ethylhexyl) cyclohexanoic acid ester, enables the production of materials having comparable mechanical properties with less PVC. It also increases UV stability, improves low-temperature properties, and reduces smoke on burning. Highly flexible and semi-rigid goods can be manufactured with these plasticizers. This film is especially suitable for the production of blood bags.

Antistatic magnetic PVC calendered film [Data from **CN105837995A**, Aug. 10, 2016.]

Raw material	Concentration, parts
PVC SG-5	30-40
Iron powder 2000 mesh particle	50-60
Calcium stearate	0.3-0.9
Propylene adipate	5-15
Antistatic agent (tris (2-aminoethyl) amine)	0.5-1.5
UV absorber	0.1-1

Antibacterial film for medical applications. [Data from Kimura, R.; Ishizuka, H.; Shibasaki, J., **US Patent 7,279,509**, Oct. 9, 2007.]

Raw material	Concentration, parts
PVC	100
Di-(2-ethylhexyl) phthalate	50
Epoxidized soybean oil	2
Zinc stearate	0.3
Calcium stearate	0.2
Zinc pyrithione	0.01
Organophosphoric ester compound	0.3

A combination of zinc pyrithione and organophosphoric ester compound forms very powerful protection against bacterial growth. This film has been invented for the production of urine bags.

Printable, self-clinging film. [Data from Nguyen, B. T.; Matsumoto, T.; Katagiri, T., **US Patent 5,698,621**, Dec. 16, 1997.]

Raw material	Concentration, parts
PVC Shintech SE-950)	100
Butyl benzyl phthalate	55
Epoxidized soybean oil (Drapex 6.8)	2
Ba/Zn stabilizer (Baerlocher UBZ-791)	2
Pigment (Violet 13)	0.07

Film containing calcium carbonate and barium sulfate. [Data from Sobieski, R T, Marshall, A, **US Patent 8,227,530**, Jul. 24, 2012, *Omnova Solutions Inc.*]

Raw material	Concentration, parts
PVC	100
Diisononyl phthalate	81
Calcium carbonate	40
Barium sulfate	75
Stabilizer	q. s.

These films exhibit exceptional strength, durability, emission and aesthetic performance properties. Significant manufacturing advantages are also observed.

4.2.2 FLOOR COVERINGS

4.2.2.1 Patented inventions

PVC composite material, foam board, and flooring [Data from Fang, Q, **US20160177579A1**, *Zhejiang Tianzhen Bamboo & Wood Development Co Ltd*, Jun. 23, 2016.]

Raw material	Concentration, wt%
PVC	56
Calcium carbonate	44
Sodium bicarbonate	0.25
Azodicarbonamide	0.15
Foam regulator PA530	4.6

PVC composite material, foam board, and flooring [Data from Fang, Q, **US20160177579A1**, *Zhejiang Tianzhen Bamboo & Wood Development Co Ltd*, Jun. 23, 2016.]

Raw material	Concentration, wt%
Toughener ACR	3.8
Stearic acid	0.5
PE wax	0.6
Calcium stearate	1.2
Zinc stearate	1.2
Titanium dioxide	1.1
Straw powder	4

Hot melt calendered wear layer for embossed substrates. [Data from Schneider, D. E.; McQuate, W. M.; Christle, P. A., **US Patent 7,378,143**, May 27, 2008.]

Raw material	Concentration, wt%
General purpose PVC	66.5
Methylmethacrylate/acrylic copolymer process aid	1.3
Acrylic release agent	0.3
Methylmethacrylate/acrylic copolymer impact modifier	3.3
Fatty acid ester lubricant	0.3
Plasticizer	26.0
Stabilizer	2.3

A melted layer is applied to a heated, embossed substrate in a manner that prevents a change of its shape and distinctiveness. The layer provides wear protection for floor covering which has a textured appearance of its substrate.

Recyclable synthetic flooring [Data from Junior, S., **WO2015028390A1**, *Tarkett Gdl S.A.*, Mar. 5, 2015.]

Raw material	Concentration, wt%
Dolomite	82.18
Recycled PVC	7.5
Epoxidized soybean oil	3.67
PVC S copolymer	2.5
Talc	2
Hydrocarbon resin	1.3
Pigment	0.85

Marble flooring. [Data from Kim, J.-K; Bahug, K.-P., **US Patent 7,306,688**, Dec. 11, 2007.]

Raw material	Concentration, parts
PVC	100
Calcium carbonate	500-650
Sepiolite, talcum, or potassium silicate	50-200
DOP	30-50
Epoxidized soybean oil	3-10
Ba/Zn stabilizer	2-6
Process additives	2-10
Pigments	quantum satis

Decorative floor covering. [Data from Son, S.-J.; Jang, H.-S.; Kang, H.-C., **US Patent 6,933,043**, Aug. 23, 2005.]

Raw material	Intermediate layer	Base layer
	Concentration, parts	
PVC (polymerization degree=1000)	100	100
Dioctyl phthalate	38	42
Calcium carbonate	90	250
Thermal stabilizer	2.5	2
Titanium dioxide	10	

There are three layers in the decorative floor covering. The second and the third layers are made from PVC with the composition given in the table above. The surface layer is made from polyethylene terephthalate film which protects decorative patterns printed by gravure printing under polyethylene terephthalate film.

Semiconducting floor covering. [Data from Soininen, P.; Peltonen, P.; Makinen, J., **US Patent 6,406,768**, Jun. 18, 2002.]

Raw material	Concentration, parts
PVC	100
2-ethylhexyl diphenyl phosphate	40
Aliphatic ester plasticizer	30
Diisodecyl adipate	10

Semiconducting floor covering. [Data from Soininen, P.; Peltonen, P.; Makinen, J., **US Patent 6,406,768**, Jun. 18, 2002.]

Raw material	Concentration, parts
Talc	50
Aluminum trihydrate	150
Titanium dioxide	2
Thermal stabilizer	2

The laminated floor covering has three layers, with top and bottom layers manufactured according to the above formulation. The middle layer is composed of a carbon fiber-glass fiber (50/50) layer which is sandwiched between the two PVC layers. The resistivity of the material is $7x10^5$ Ω.

Floor covering with enhanced low temperature flexibility. [Data from Grass, M, Becker, H G, **US Patent 2013/0317153**, Nov. 28, 2013, *Evonik Oxeno GmbH*.]

Raw material	Concentration, parts
PVC (SilVin S 271)	100
Diisononyl phthalate	53
Calcium carbonate (Omya BSH)	80
Thermal stabilizer (BP MC KA 83/S)	4

4.2.3 POOL LINER

4.2.3.1 Formulation proposed by raw materials suppliers

Akcros Chemicals developed several thermal stabilizers, which are suitable for demanding applications such as pool liners. The following stabilizers can be used for this application: Lankromark LZB567, LZB600, LZB655, and LZC803. Galata Chemicals proposed the following stabilizers: Mark 4716, Mark 4727, and Mark 6710ACM. Baerlocher proposed calcium-zinc MC 8763-3 CP.

4.2.3.2 Patented inventions

Pool liner. [Data from Stevenson, D. R.; Harr, M. E.; Jakupca, M. R., **US Patent 6,824,711**, Nov. 30, 2004.]

Raw material	Concentration, parts
PVC	100
Plasticizer	45
Epoxidized soybean oil	5
Calcium carbonate	20
Stearic acid	0.25

Pool liner. [Data from Stevenson, D. R.; Harr, M. E.; Jakupca, M. R., **US Patent 6,824,711**, Nov. 30, 2004.]

Raw material	Concentration, parts
Alkyl bisphenol-A phosphite (Doverphos 675)	2.7
Tetraphenyl diphosphite (Doverphos 11)	0.65
Zinc octanoate	0.15

The phosphite esters function in this formulation as primary heat stabilizers by replacing labile chlorines on PVC *via* the Arbuzov rearrangement mechanism. When phosphites are used at optimized levels in combination with catalytic amount of zinc and normal level of epoxidized soybean oil, they provide excellent early color and adequate long-term stability to flexible PVC compounds. Their use also helps in lowering stabilization cost, elimination of toxic metals, elimination of plate out, poor printability, viscosity drift in plastisols, haze, bloom, water blush, and staining.

Insecticidal pool liner. [Data from Breitscheidel, B, Ishaque, M, Harmsen, S, Wagner, J, **World Patent WO2010069796**, Jun. 24, 2010. *BASF*.]

Raw material	Concentration, parts
PVC	100
5 wt% solution of α-cypermethrin in diisononyl phthalate	30
Barium-zinc stabilizer	3

Polymer composition comprises a polymer, a plasticizer, an insecticide and/or an insect repellent.

Laminated patterned liner [Data from Rosario, P, **US20160263870A1**, *Constant Services Inc*, Sep. 15, 2016.]

PVC pool liner has been imprinted with a decorative pattern to mimic the appearance of a decorative tile. It is advantageous to design PVC pool liners to be protected from degradation. The decorative pattern is protected from degradation by external factors by an upper laminated layer.

4.2.4 ROOFING MEMBRANE

4.2.4.1 Formulation proposed by the raw material suppliers

Clear calendered sheet. [Data from **Mark 2270**. Technical data sheet. *Crompton*.]

Raw material	Concentration, parts
PVC (K-61)	100
Ester type lubricant	1-1.5
Acrylic process aid	2-3
MBS impact modifier	10-15
Mark 2270 (butyltin carboxylate/mercaptide)	1.5-2.5
Toner pigment	quantum satis

Starting formulation including Elvaloy. [*DuPont*]

Raw material	Concentration, parts
PVC	100
DIDP	30
Elvaloy KEE	30
ESO	3
Stabilizer	3
TiO_2	15
UV stabilizer	1-1.5
Calcium carbonate	15
Lubricant	0.5-1

4.2.4.2 Formulations found in the open literature

Generic formulation of roofing membrane. [Data from Paroli, R. M.; Dutt, O.; Delgado, A. H.; Stenman, H. K., *J. Mater. Civil Eng.*, **5**, 1, 83-95, 1993.]

Raw material	Concentration, wt%
PVC	55
Plasticizers	28
Fillers	7
Pigments	5
Process oils and biocides	3
Stabilizers	2

Roofing membrane with NOR-HALS. [Data from Capocci, G.; Hubbard, M., *J. Vinyl Additive Technol.*, **11**, 3, 91-94, 2005.]

Raw material	Concentration, parts
PVC	100
Process aid	0-2.5
Monomeric plasticizer(s)	60-70
Epoxidized soybean oil	5-8
Biocide	1-3.5
Thermal stabilizer	4-6
Calcium carbonate	0-15
Titanium dioxide	10-13
UV stabilizer (NOR HALS 833)	1

Use of UV stabilizer permits 50% retention of elongation after 8000 hrs in Weather-O-Meter. The same stabilizer is proposed for application in geomembranes, PVC coated fabrics, flooring, wallcoverings, automotive trim.

4.2.4.3 Patented inventions

Impact resistant roofing membrane. [Data from Mehta, N R, Flath J C, Pettey, D A, **World Patent WO2009143432**, Nov. 26, 2009, *Cooley Group Holdings Inc.*]

Raw material	Concentration, wt%
PVC	51
TiO_2	6
Calcium carbonate	3
Phthalate plasticizer	30
Epoxidized soybean oil	2
Oxybisphenoxyarsine (10%)	1
Antioxidant (Irganox 1076)	0.3
HALS (Tinuvin 622 LD)	0.2
Antimony oxide	3
Ba-Zn stabilizer	3
Oxidized polyethylene	0.5

4.2.5 SHEET

4.2.5.1 Formulation proposed by the raw material supplier

Clear sheet. [Data from **Thermolite 108**. *Arkema*.]

Raw material	Concentration, parts
PVC (K=60)	100
Thermolite 108	0.6-1.2
Internal lubricants	1.2-1.5
External lubricants	0.1-0.5
Plastistrength 550	1.5-2
Plastistrength 710	0.7-1
Clearstrength 303H	6-12
Toner	quantum satis

4.2.5.2 Patented inventions

Sheet flooring compound. [Data from Kauffman, W. J.; Christle, P. A.; Saporetti, W. B.; Hynicka, S. F.; Wright, R. W., **US Patent 6,511,926**, Jan. 28, 2003.]

Raw material	Base	Foam	Wear
	Concentration, wt%		
PVC (general purpose or scrap, K=66)	25.9		
Primary phthalate plasticizer	10.5	22.6	15.9
Epoxidized soybean oil	0.8	0.7	12.8
Ca/Zn stabilizer	1.3		1.7
Acrylic process aid	1.5		
Limestone filler	60	12.6	
PVC foam dispersion resin		31.5	69
PVC blending resin		25.7	
Titanium dioxide		3.2	
Activated blowing agent		0.9	
Hydrocarbon diluent		0.7	

Flooring material. [Data from Nakano, R., **US Patent 5,772,941**, Jun. 30, 1998.]

Raw material	Concentration, parts
PVC (polymerization degree=1050)	100
Chopped glass fiber (8 mm long, 6 μm in diameter)	3-30
Diethylhexyl phthalate	24
Epoxidized soybean oil	3
Ba/Zn stabilizer	2.5
Modifier	1.5

The formulation is useful for the production of sheets by calendering (on a four roll calender equipped with an embossing machine). The sheet manufactured has an excellent scratch, wear, and slip resistance, and it is suitable for use as a flooring material.

Sheet with improved heat resistance and mechanical performance by use of crosslinking plasticizer. [Data from Kyriyama, K.; Ichihara, M.; Sugawara, R. S.; Hirakata, K. H., **US Patent 4,402,887**, Sep. 6, 1983.]

Raw material	Concentration, parts
PVC (polymerization degree=1050)	100
Reactive plasticizer (trimethylolpropane triacrylate)	50
Photosensitizer (benzoin isopropyl ether)	0.5
Polymerization inhibitor (t-butylhydroquinone)	0.5
Thermal stabilizer (dibutyltin maleate)	1.5

Example of effective stabilization of calendering formulation. [Data from Krainer, E.; Bacaloglu, R.; Shah, M.; Fisch, M. H.; Frenkel, P.; Bae, K. J., **US Patent 7,282,527**, Oct. 16, 2007.]

Raw material	I	II
	Concentration, parts	
PVC (Oxy 225)	100	100
DIDP	45	45
Epoxidized soybean oil	5	5
Ca stearate	0.5	0.5
Organic phosphite	1	1

Example of effective stabilization of calendering formulation. [Data from Krainer, E.; Bacaloglu, R.; Shah, M.; Fisch, M. H.; Frenkel, P.; Bae, K. J., **US Patent 7,282,527**, Oct. 16, 2007.]

Raw material	I	II
	Concentration, parts	
Antioxidant	0.3	0.3
Ba/Zn stabilizer	1.5	
Weston EHDP (Crompton)		1
Polyethylene glycol 200		1
60% $NaClO_4$ * H_2O		0.345

Sheet with optimized external lubricant. [Data from Lindner, R.; Clarke, V., **US Patent** 5,414,035, May 9, 1995.]

Raw material	Concentration, parts
PVC	100
Modifier	5
Thermolite 831	1.25
Thermolite 890	1.25
Loxiol G16	0.875
A-C 307 polyethylene	0.125

Heat-insulating transparent PVC sheet [Data from Shieh, S-Y; Fung, D-R; Huang, Y-T; Lin, C-H; Cheng, C-H; Wu, W-Y, **US8257632B2**, *Nan Ya Plastics Corp*, Sep. 4, 2012.]

Raw material	Concentration, parts
PVC	100
DINP	40
Ba/Zn stabilizer	3
Stearic acid	0.4
Colorant	0-12
CeB_6	2.5
Coupling agent	0.8
UC absorber	0.8

4.2.6 SPONGED LEATHER

4.2.6.1 Formulation proposed by the raw material supplier

Calendered sponged leather. [Data from **Mark K 136**. Technical data sheet. *Crompton*. June 1999.]

Raw material	Concentration, parts		
S-PVC (K=60-63)	100		
S-PVC (K=64-67)		100	
S-PVC (K=68-71)			100
DOP	35	55	80
Mark K 136 (Ba/Zn stabilizer)	1.5	1.3	1.2
Zinc oxide	0.2	0.3	0.4
Barium stearate	0.5	0.35	0.25
Azodicarbonamide	2.5-4.0		
Calcium carbonate	10-30		
Stearic acid	0.1-0.2		
Pigments	quantum satis		

Mark K 136 in combination with zinc oxide and barium stearate stabilizes the formulation and acts as a kicker, giving a very fine homogeneous cell structure. Production of sponge leather is a two-stage process in which calendering is done at 155-180°C and foaming takes place in a heating channel at 200-230°C.

4.2.7 CONCLUSIVE REMARKS

The typical formulation used in the production of the calendered film includes the following raw materials:

- PVC (medium to high molecular weight)
- plasticizers (most frequently phthalates)
- fillers (most frequently calcium carbonate)
- lubricants (stearic acid and stearates are the most popular)
- thermal stabilizers (metal soaps dominate)
- secondary thermal stabilizers (epoxidized oils, phosphites, and Na perchlorate)

Many other additives are used depending on film application and its expected properties. These include:

- antibacterial additives or biocides/fungicides (for medical and outdoor applications)
- insecticide (pool liner)
- flame retarding additives (aluminum trihydrate, antimony trioxide, and phosphoric acid plasticizers)
- acrylic polymer resin (improvement of mechanical properties)

- gloss improving compounds
- antiblocking and slip additives
- lubricants for special needs (PE wax, ester lubricants)
- UV stabilizers (HALS, phosphites, antioxidants)

Calendered floor coverings use in addition to the above additives:

- acrylic process aid
- acrylic release agents
- acrylic impact modifiers
- blowing agents and matching kickers

In roofing membranes, UV stability is of the highest concern, and it is still a work in progress. In the past, UV absorbers were suggested but never proven to be useful. NOR-HALS and higher concentrations of phosphites but full evaluation is still not available.

Many important properties are formulation controlled:

- stain resistance (stabilizer type)
- VOC emission (liquid components (type and quantity), such as plasticizers, stabilizers, viscosity reducers, etc.)
- antistatic properties (use of special additives)
- electrical conductivity (use of special additives or inclusion of conductive layer)
- dimensional stability (PVC molecular weight, type and amount of plasticizers, blending)
- appearance (contamination, lubrication, and rheological properties)
- high gloss (special additives)
- color (thermal stability, use of brighteners)
- thermal stability (type and concentration of stabilizers and costabilizers vs. process conditions)
- UV stability (damage done during processing, selection of thermal and UV stabilizers)
- printability (surface properties)
- adhesion between film layers (type and amount of slip and antiblocking additives)
- abrasion resistance (concentration of plasticizers, fusion conditions, concentration and type of fillers, and the structure of material)

Some problems in production quality and output are formulation controlled and these include:

- pinholes (foreign matter, poor mixing, or presence of unplasticized particles)
- water-marking (lubricant contamination)
- blooming (insufficient mixing, selection of lubricant, selection of pigment)

- blocking (insufficient concentration or the wrong type of antiblocking additives)
- air bubbles (presence of volatiles in the formulation, very likely water which has to be removed by drying)
- fish-eyes (contamination by foreign objects, mixing of resins of different grades, or insufficient dispersion of filler)
- color change (inadequate stabilization)
- migration (too much plasticizer, incompatible plasticizer, insufficient mixing)

4.3 COMPOSITES

Composite is a structural material that gains its strength from a combination of complementary materials, i.e., polymer and its reinforcement. The most common type of composite, glass fiber reinforced material, is not a typical example in the case of PVC because of difficulties in design for interaction between both materials and lack of convenient means of adhesion promotion.

But PVC forms many composite materials with particulate and fibrous fillers. Cellulose fiber and newsprint recycled fiber are two typical examples of fibrous materials. The list of powders is longer, including talc, mica, clay, wood flour, carbon black, glass beads, hydrotalcite, alumina trihydrate, polypyrrole, and various nano-materials including nano-calcium carbonates.

The effects of composite formation are not only restricted to the improvement of mechanical properties, such as toughness, tensile strength, and many other, but also include, improvement of thermal and electric conductivities (carbon black, polypyrrole), reduction of water migration (platelet fillers such as talc and mica), improvement fire resistance (alumina trihydrate), improvement of quality (wood-like feel with wood filler), and decorative value.

4.3.1 FORMULATION PROPOSED BY THE RAW MATERIAL SUPPLIER

Wood/PVC composite [Data from Arkema. Hajji, P., PVC Conference, Brighton, 2008.]

Raw material	Concentration, parts
PVC K57 (Lacovyl SO71)	100
Thermolite T890F (octyl tin mercaptide)	1.8
Ca stearate	1.5
Process aid (Plastistrength 770)	1
Process aid (Plastistrength 530)	2
Acrylic impact modifier (Durastrength 320)	7
External lubricant (paraffin wax)	1
Wood flour (Lignocel S150TR) (150-200 μm)	

4.3.2 FORMULATION FOUND IN THE OPEN LITERATURE

PVC composite with increased stiffness and toughness by incorporation of ultrafine talc. [Data from Wiebking, H. E., *J. Vinyl Additive Technol.*, **2**, 3, 187-189, 1996 and Wiebking, H. E., *J. Vinyl Additive Technol.*, **12**, 1, 37-40, 2006.]

Raw material	Concentration, parts
PVC (K=66)	100
Methyltin stabilizer	1.25
Acrylic process aid	1
Calcium stearate	1.2
Paraffin wax	1.25
Polyethylene wax	0.2
Acrylic impact modifier	5
Ultrafine talc	20

Addition of talc significantly increases the flexural modulus of PVC. Also, stiffness and toughness are increased. The impact strength can be maintained by use of the appropriate type and concentration of impact modifier.

Some other examples of formulations of PVC composites are given in the next section.

Glass fiber filled wood/PVC composite. [Data from Tungjitpornkull, S, Sombatsompop, N, *J. Mat. Process. Techn.*, **209**, 3079-88, 2009.]

Raw material	Concentration, parts
Suspension PVC (Siamvic 258RB)	100
Pb-Ba-based organic stabilizer	3.6
Finalux lubricant	0.6
Calcium stearate	0.9
Calcium carbonate	12
Amino-silane	1
Wood sawdust	50
E-chopped strand glass fiber	6-17

Wood/PVC composite [Data from Pulngern, T.; Chitsamran, T.; Chucheepsakul, S.; Rosarpitak, V.; Sombatsompop, N., *Constr. Build Mater.*, **111**, 1914-8, 2016.]

Raw material	Concentration, parts
PVC K=66	100
Thermal stabilizer (TS-DBL-Pb-Ba)	3.6
External lubricant (Finalux G-741)	0.6
Calcium carbonate (Omyacarb-2T)	9
Calcium stearate	0.3
Acrylic process aid (PA20)	8
Wood particle (100-300 μm)	100
N-2 (aminoethyl) 3-aminopropyl trimethoxysilane	1 wt% of wood

4.3.3 PATENTED INVENTIONS

PVC nanocomposite. [Data from Jacobsen, H, Sterky, A K S, **European Patent EP2428531**, Mar. 14, 2012, *Ineos Norge Holdings AS.*]

Raw material	Concentration, parts
PVC (S6575) with silica	100
Mark 17 MOK	2
ESO	0.7
Allied AC 316A	0.2
Loxiol G72	0.4
Loxiol G60	1
Paraloid K120N	0.6

Nanocomposite has impact strength increased by 80-90%.

Foam composite wood replacement material. [Data from Zehner, B. E., **US Patent**, **6,590,004**, Jul. 8, 2003.]

Raw material	Concentration, parts
PVC	100
Cellulosic filler	54
Thermal stabilizer	3
Process aid	9
Lubricant	3

Extrudable profile from PVC-wood fiber composite. [Data from Seethamraju, K. V.; Heikkila, K. E.; Deaner, M. J., **US Patent 6,210,792**, Apr. 3, 2001.]

Raw material	Concentration, parts
PVC (Geon 427)	100
Methyltin mercaptide (Advastab TM 181)	2
Paraffin wax (XL 165)	0.5
Oxidized polyethylene (AC-629-A)	0.8
Vinyl chloride-vinylacetate-glycidyl methacrylate copolymer with epoxy functionality (VERR40)	6
Saw dust	40

Sound attenuation composite. [Data from Veiga, M. J.; Satin, R. J., **US Patent 5,622,662**, Apr. 22, 1997.]

Raw material	1st layer	2nd layer
	Concentration, wt%	
PVC (Geon 178)	12.19	13.12
PVC (Formolon 40)	2.44	2.63
Pigment paste (TPG 10 green)	0.99	
Aluminum flake (Grade 2000)		0.49
Flammability additive (Thermoguard CPA)	0.73	0.79
Surfactant (Triton 114)	1.07	1.15
Plasticizer (H-150)	9.6	10.41
Mineral spirits	2.68	0.86
Barium sulfate	61.57	66.28
Microspheres (K-1)	1.27	
Thermal stabilizer (Thermchek 1776)	0.47	0.47
Thermal stabilizer (Thermchek 904)	0.15	0.16
Flame retardant (Frysol CEF)	1.49	1.60
Flame retardant (hydrated alumina)	1.47	1.57
Adhesion promoter (Desical)	0.44	0.47
Froth stabilizer (Silicone DC surfactant 1250)	3.47	

Multilayer louver with a polished metal look. [Data from Hawrylko, R. B.; Lakstigala, K.; Asgaralli, A. A., **US Patent 5,496,630**, Mar. 5, 1996.]

Raw material	Concentration, parts
PVC	100
Acrylic process aid	1.75
Epoxidized soybean oil	5
Thermal stabilizer (dimethyltin diisooctyl thioglycolate)	1.8
Aluminum flake (Silvex 540 series)	0.5
Aluminum flake (Sparkle silvex)	0.6
Stearic acid	0.5
MBS impact modifier	6
Oxidized polyethylene wax	0.15
Paraffin wax	0.05
Pearl (Afflair 235)	0.1
Pearl (Afflair 135)	0.1
Pigments	quantum satis

Plastic stone composite [Data from Zheng, J. G., **US20160207835A1**, *Wei-Teh Ho*, Jul. 21, 2016.]

Raw material	Concentration, parts
PVC resin SG-9	50
Coarse whiting powder (particle size 600 mesh)	70
Calcium/zinc stabilizer	3
Polyethylene wax	0.5
Chlorinated polyethylene	2.5
stearic acid	0.8
Dioctyl phthalate	2
ACR processing aid	1.6

4.3.4 CONCLUSIVE REMARKS

Production of composite material usually requires complex formulation and production technology. The following groups of raw materials are used:

- PVC (medium to high molecular weight)
- impact modifiers (acrylic and MBS)
- filler or fiber reinforcements (cellulosic fibers, sawdust, ultrafine talc)
- lubricants and rheology modifiers (paraffin wax, polyethylene wax, oxidized polyethylene, calcium stearate, acrylic process aid)
- property modifying fillers (microspheres, barium sulfate)
- flame retardants (organic and inorganic)
- adhesion promoters

It is important to note that plasticizers are rarely used which is logical since composite materials are produced to have improved mechanical strength. The most important properties of composite materials include:

- impact strength
- flexural modulus
- stiffness and toughness

Processing, in most cases without plasticizers and with high loads of fillers and fibers, requires:

- excellent lubrication to lower high shear stress
- excellent thermal stabilization because the material is exposed to high mechanical and thermal stresses

Other important requirements include:

- adhesion between fillers and fibers (glass fiber reinforcement is rarely used in PVC composites because of difficulties in increasing adhesion between polymer and fiber; without adhesion, composite properties are not substantially improved by reinforcing fibers)
- many applications that require flame resistance and flame retardants have to be used to compensate for the flammable additives. Considering that plasticizers are rarely used, it is easy to obtain flame resistant composites with small concentrations of flame retardants
- if the density of composite is important, it can be decreased by the addition of hollow microspheres and it can be increased by the addition of barium sulfate and many other fillers having high density. In one application reported above, barium sulfate was used for sound attenuation

Most composites are produced by extrusion or injection molding; therefore troubleshooting methods should be related to the processing method and reviewed using information in respective sections below.

4.4 DIP COATING

Dip coating includes two processes of hot and cold dipping. In hot dipping, the mold is heated to a required temperature, and it is then immersed in a coating mixture (usually PVC plastisol) for a prescribed amount of time, after which the mold is withdrawn from the coating mixture and material is gelled in an oven. This method is used for the production of handles and grips, usually for tools and bicycles, hangers, and gloves. It can be easily predicted that mold temperature and time of immersion determine the amount of coating. Plastisol formulation and rheology are essential but not as critical as they are in cold dipping. Hot dipping is also known under the name of dip molding.

In cold dipping, the mold is cooled to room temperature, and it is immersed in plastisol, withdrawn, and taken to an oven for gelation. Here, we need to fulfill several important requirements. When the mold is being immersed in or withdrawn from plastisol, it is done with relatively high speed to shorten the process time. It is thus required from plastisol that it has low viscosity at the high shear rate. After the mold is withdrawn from plastisol, plastisol still flows but the shear rate of flow is low, and under these conditions, the viscosity should rise rapidly to permit a certain accumulation of plastisol on the mold's surface. The rheological properties of plastisol which accommodate both low and high viscosities at different shear rates are called pseudoplasticity. The more complex rheological behavior requires more complex formulations or methods of preparation. Complex rheological behavior can be facilitated by selection of appropriate grades of PVC or their combinations, use of a combination of plasticizers, proper stabilizers, and rheological additives. It is also possible to modify the rheology of plastisol by controlled heating during mixing. Cold dipping method is usually used for materials that use a mold which cannot be preheated. Typical products include textile supported gloves, wire baskets, frames, and table and chair legs.

Both methods of dip coating have been used for a very long time because they are very economical for the manufacture of products involved. The methods were thus perfected a long time ago.

4.4.1 PATENTED INVENTIONS

Antimicrobial gloves. [Data from Nishi, Y.; Miyake, A., **US Patent 6,012,169**, Jan. 11, 2000.]

Raw material	1st layer	2nd layer
	Concentration, parts	
PVC (polymerization degree = 1,500)	100	
DOP	90	
Co-stabilizer (epoxidized soybean oil)	3	
Stabilizer (Ca/Zn)	3	
Thickener (SiO_2)	0.2	
Methylmethacrylate copolymer		3.327
Surfactant		0.16
Thickener		0.4
Antiseptic agent		0.08
Antimicrobial agent (Ag-zeolite)		0.033
Water		96

This process has several stages. In the first stage, the mold is heated to 70°C. In the second stage, the mold is immersed in plastisol; after withdrawing, plastisol is cured in a 250°C oven for 60 sec to fabricate a 0.1 mm thick layer of PVC. The mold is then immersed in methylmethacrylate copolymer emulsion and after withdrawing from solution heated for 10 min. in a 200°C oven. A 5 μm thick layer is formed. The glove is then stripped from the mold and inverted; thus the antimicrobial layer is inside the glove.

PVC coated gloves. [Data from Ahmed, S U, Ahmed, R R, Kassim, M, **European Patent EP2527123**, Nov. 28, 2012, *Midas Safety Inc.*]

Raw material	Concentration, parts
Pevikon P737 (paste making PVC)	83
PVC Resin SPRD (VC/VA copolymer, blending resin)	17
Palatinol AH (plasticizer, DOP)	96.87
Santicizer 160 (plasticizer, BBP)	19.8
Calcium stearate	2
Mark 1495C (heat stabilizer)	1.5
Epoxidized soybean oil	5
Aerosil 200 (thickener)	0.1
Agitan 6236M (viscosity adjuster, antifoam)	0.1
Pigment	0.83

Antimicrobial gloves. [Data from Mixon, G. C., **US Patent 5,906,823**, May 25, 1999.]

Raw material	Concentration, wt%
PVC	46
Diisononyl phthalate	48
Ca/Zn stabilizer	3.7
Antimicrobial agent (triclosan)	0.3

Here a single layer glove material contains an antimicrobial agent which migrates to the surface of the glove to perform its functions.

Protective work gloves. [Data from Dunmire, R. W.; Miller, D. J.; Johnson, M. D., **US Patent 4,519,098.**]

Raw material	Concentration, parts
PVC	100
DOP	122
Stabilizer	0.8
Filler	20

The above formulation is cold applied on the surface of adhesive (a rubber layer which has been previously applied to cotton textile). The first dip of PVC plastisol may be followed by the second dip in the same or different plastisol, e.g., PVC foam (not given in the patent). If such is the case, the mold with the glove undergoes treatment in a 188-205°C oven for 1-1.5 min after the first layer of PVC was applied, then the complete glove is gelled in the 188-199°C oven for 15-20 min. It is quite apparent that the process is time-consuming in this older technology.

Gloves having rough surface [Data from Ahmed, S. U.; Ahmed, R. R.; Kassam, M., **EP2527123B1**, *Midas Safety Innovations Ltd*., Dec. 16, 2015.]

Raw material	Concentration, parts
PVC (Pevicon P737)	83
VC/VA (SPRD)	17
Plasticizer (Palatinol AH, DOP)	96.87
Plasticizer (Santicizer 160, BBP)	19.8
Stabilizer (calcium stearate)	2

Gloves having rough surface [Data from Ahmed, S. U.; Ahmed, R. R.; Kassam, M., **EP2527123B1**, *Midas Safety Innovations Ltd*., Dec. 16, 2015.]

Raw material	Concentration, parts
Heat stabilizer (Mark 1495C)	1.5
Stabilizer (epoxidized soybean oil)	5
Thickener (Aerosil 200)	0.1
Viscosity adjuster (Agitan 6236M)	0.1
Pigment	0.83

Plastisol with high rubber content. [Data from Breton, F. J.-M., **US Patent 6,054,524**, Apr. 25, 2000.]

Raw material	Concentration, parts
Nitrile rubber (e.g., Chemigum P35)	40
Aliphatic solvent (e.g., Isopar G or Dowanol MP)	20
DOP	100
PVC	100
Dibutyltin dilaurate	3

The order of addition was as given in the table, meaning that first nitrile rubber was dissolved in the aliphatic solvent, followed by the addition of plasticizer, before PVC and its thermal stabilizer were added. The plastisol formulation is suitable for the production of gloves, shoes, boots, tool handles and wire goods, such as dishwasher racks, dish drainer baskets, and napkin holders.

Medical glove. [Data from Horwege, K. S.; Reuck, D. L.; Pot, M. Y., **US Patent 5,881,386**, Mar. 1999.]

Raw material	PVC layer	PU layer
	Concentration, wt%	
PVC (Geon 121X10)	8.2	
PVC (NV2 Formolon)	42.3	
Plasticizer (Jayflex DINP)	43.4	
Viscosity modifier (paraffin oil, Jayflex 215)	1.9	
Epoxidized tall oil (Drapex 4.4)	1.5	
Thermal stabilizer (Interstab LT-4468)	2	
Viscosity modifier (polyether glycol, Deplastol)	0.4	

Medical glove. [Data from Horwege, K. S.; Reuck, D. L.; Pot, M. Y., **US Patent 5,881,386**, Mar. 1999.]

Raw material	PVC layer	PU layer
	Concentration, wt%	
Pigment	0.3	
Polyester polyurethane emulsion (Solucote 10511I-3-35)		15
Slip agent (oxidized PE emulsion, Polyemulsion OA3N30)		8
Silica (Cabosperse A3875)		6
Calcium carbonate (Duramite)		1
Viscosity modifier (xantan gum, Ketrol RD)		0.1
Antifoam agent (Bubble breaker 625)		0.1
Surfactant (aliphatic polyether, Antranox LF330)		0.5
Water		q.s.

A mold having the form of a hand has its outside surface heated to a temperature between 70 and 95°C and it is dipped into a PVC plastisol bath maintained at 35 to 45°C, forming a PVC plastisol film on its surface. The mold having the film on its surface is removed from the first bath, allowed to drain, then it is heated in an oven to raise the temperature of the film on the surface to between 160 to 195°C, forming a gelled and fused film with an average thickness of about 0.08 mm. The film is cooled to 75-90°C and dipped in a second bath maintained at a temperature 35-45°C containing an aqueous emulsion including polyurethane, a slip agent, and a texturizing agent to form a second film layer over the first layer. The mold having the first and second films is removed from the second bath and allowed to drain, then it is heated to 70-90°C to dry and adhere the second layer to the first layer, forming a unified structure. A cuff is then formed on the unified structure which is then stripped and reverted, forming a glove.

The polyurethane side is in contact with the user, and the PVC side is in contact with the patient.

Plastisol with crosslinked rubber. [Data from Ngoc, H. D., **US Patent 5,739,203**, Apr. 14, 1998.]

Raw material	Concentration, parts
Crosslinked nitrile rubber	20
Antioxidant (Wingstay K)	0.2
DOP	85
PVC	100
Thermal stabilizer	3

The highly crosslinked nitrile rubber is synthesized according to the invented method (fully disclosed in the patent). Nitrile rubber was dispersed in hot DOP (25-80°C) before PVC and its stabilizer were added. The rubber containing plastisol was designed with the manufacture of gloves, shoes, and boots in mind.

Plastisol containing polyurethane or polyurea. [Data from Petit, D.; Lazdang, M., **US Patent 5,428,087**, Jan. 27, 1995.]

Raw material	Concentration, parts
PVC (Solvic 372HA)	100
Benzyl butyl phthalate	90
Epoxidized soybean oil	10
Ba/Cd stabilizer (now obsolete)	0.5
Polyol (poly-ε-caprolactone, CAPA 316)	48
Blocked diisocyanate (IPDI 1540)	52
Catalyst (dibutyldilauryl sulfate, DABCO T12)	0.5

Soft, strong plastisols [Data from Murnahan, E. B.; Tresino, J. J., **WO2014028481A1**, *PolyOne Corporation*, Feb. 20, 2014.]

Raw material	Concentration, parts
PVC resin (PVC 172)	18-22
Plasticizer(s) (dioctyl adipate)	24-27
Trimethylolpropane trimethacrylate	48-52
Stabilizer(s) (Plastistab 2335, Ba/Zn), OMG 2932	0.5-1
Thickener (fumed silica and/or Ircogel 903)	2.5-3
Pigment(s)	0.1-0.2
Moisture scavenger(s) (Polycal OF325)	0.08-0.12

The idea of this invention is to improve resistance to heat and solvents by application of polyurethane system which is not reactive at room temperature but reacts during the gelling process because blocked isocyanate is unblocked at elevated temperature. The plastisol has stable viscosity for 10 days. The plastisol and technology can be used for many different purposes, including dip coating.

Plastic bait killing crop pests. [Data from McKibben, G.H.; Dickens, J. C.; Smith, J. W., **US Patent 5,290, 556**, Mar. 1, 1994.]

Raw material	Concentration, wt%
PVC	53.29
DOP	35.60
Lauric acid ester of phytol (feeding simulant)	4.5
Grandlure (sex pheromone)	0.214
Titanium dioxide (pigment)	5.4
Propoxur	1

The bait was prepared by a dip molding process in which steel rods heated to 182°C were dipped into the plastisol for about 25 s and cured in an oven at a temperature of 170-190°C, after withdrawing it from plastisol.

Dip molding formulation to manufacture products which do not stick to each other. [Data from Nakayama, Y.; Murase, Y., **US Patent 5,248,723**, Sep. 28, 1993.]

Raw material	Concentration, parts
Blending resin (invented product discussed below)	50
Paste resin (Vinika P450, PVC)	50
Di-n-octyl phthalate	60
Tin stabilizer (T-17MJ)	3
Pigment	1

Blending resin is obtained from emulsion polymerization of vinyl chloride in the presence of gelatin, polyvinyl pyrrolidone, diallyl phthalate, sodium dodecylbenzene sulfonate, tert-butyl pivalate, and disodium hydrogen phosphate. The surface of this product has a very limited light reflection, and it does not stick to the same product.

Molded medicinal instrument (stethoscope). [Data from Packard, T. J.; Quackenbush, J. H., **US Patent 5,111,904**, May 12, 1992.]

Raw material	Concentration, parts
PVC	100
Butyl benzyl phthalate	60-70
Dialkyl phthalate	15-25
Epoxidized soybean oil	3-7
Heat stabilizer	2-5
Pigment	2-4

4.4.2 CONCLUSIVE REMARKS

Compositions for hot dipping are usually more straightforward to formulate because they require less attention to rheological properties than cold dipping formulations. The following are the significant components of formulations:

- PVC low to medium grades
- plasticizer(s) usually used at larger concentrations for cold dipping (90-110 phr), and less plasticizer (50-100) can be used for hot dipping (depending on coating thickness)
- thermal stabilizers are usually Ca/Zn carboxylates, but tin stabilizers are also in use
- epoxidized oils are used as costabilizers, considering that fusion requires extended heating
- many rheological additives can be used but fume silica and paraffin oil are the most popular (xanthan gum in water-based formulations)
- some formulations are based on polymer mixtures, including nitrile rubber crosslinked and non-crosslinked and polyurethanes which are added into plastisol or used as an additional coat (usually to reduce adhesion of gloves to hands)

Some other compounds are added to formulations to achieve specific special requirements. These additives include:

- antiseptic and antimicrobial agents (e.g., Ag-zeolite or triclosan), especially in gloves and other products for medical applications
- slip agents
- antifoam agents

The most important properties of these formulations include:

- rheology – supporting the formation of a layer of uniform thickness as per requirements and preventing dripping and droplet formation at the bottom of the form
- good thermal stability (fusion process may take up to 15 min at 200°C),

- low modulus and high elongation

The following problems related to formulation occur during production:

- sagging, dripping (rheological properties have to be adjusted to take advantage of pseudoplastic behavior)
- cratering, pinholes, bubbles (water in resin or additives, impurities, porous substrate)
- coat thickness different than required (viscosity and overall rheological properties have to be adjusted)
- shelf life of plastisol (causes: storage at too low temperature, thixotropic properties, too high temperature and natural aging; in the first two cases gentle stirring and equilibration to room temperature usually restores properties; storage at excessively high temperatures (above room temperature) usually causes irreversible changes; natural aging (length of time) depends on formulation usually in the relationship with plasticizer type and proper mixing of rheological additives)

4.5 EXTRUSION

Extrusion is the most common method of PVC processing, mainly because of large scale production of profiles used in the manufacture of windows and doors and other construction supplies. Various groups of products are discussed in separate sections which follow, the first, the General Section, which includes patent literature on the application of various additives which are of general interest in extrusion processing. The General Section also consists of some patents showing the first application of various important additives used today.

4.5.1 GENERAL SECTION

4.5.1.1 Patented inventions

Properties of efficient plasticizers with improved properties. [Data from Gosse, C.; Larson, M.; Legrand, P. J. P.; Caers, R. F.; Daniels, P. H.; Godwin, A. D.; Naert, D., **US Patent 7,413,813**, Aug. 19, 2008.]

Property	DOP	DEHCH	DINP	DINCH	DIDP	DIDCH
Viscosity at 20°C, mPas		45.5		64.7		87.0
Density at 20°C, g/cm^3		0.955		0.946		0.943
Water content, ppm		64		111		69
Acid value, mg/g KOH		0.03		0.03		0.04
Shore A*	81.5	81.8	85.0	86.3	86.2	89.1
Shore D*	31.1	31.5	34.9	36.0	36.6	38.9
Thermal stability, min at 180°C*	33	32.3	28.5	30	28.5	30.8
Modulus at 100%, N/mm^2 **	10.9	11.4	10.7	10.5	11.2	10.4
Stress at break, N/mm^2 **	15.6	14.5	15.1	14.9	16.0	13.5
Elongation at break, % **	301	223	289	290	299	235
Weight loss (7 days at 100°C), %	0.79	2.49	0.35	0.72	0.27	0.38

DOP - di-(2-ethylhexyl) phthalate, DEHCH – C_8 alcohol ester of cyclohexanoic acid, DINP – diisononyl phthalate, DINCH – diisononyl ester of cyclohexanoic acid, DIDP – diisodecyl phthalate, DIDCH – C_{10} alcohol ester of cyclohexanoic acid; *(PVC 100, plasticizer 50, $CaCO_3$ 10, LZB 320 2); **(PVC 100, plasticizer: DOP 50, DEHCH 50, DINP 53, DINCH 54.5, DIDP 55, DIDCH 57.5, LZB 722 2, ESBO 0.5)

High flame retardant composition. [Data from Fung, D-R, Liao, T-C, Wang, S-H, **US Patent US20100292379**, Nov. 12, 2010, *Nan Ya Plastics Corporation*.]

Raw material	Composition, parts
PVC	100
Calcium-zinc stabilizer	0.5
Trioctyl trimellitate	20
Polyethylene wax (lubricant)	0.2
Chlorinated polyethylene elastomer (toughening)	25
Aluminum hydroxide	100
Zinc borate	5
Molybdenum trioxide	5
Montmorillonite	2
Vinyltrimethoxysilane	2
Dicumyl peroxide initiator	0.1

Efficient stabilizing systems. [Data from Friedrich, H.-H.; Kuhn, K.-J.; Wehner, W.; Hopfmann, T., **US Patent 7,393,887**, Jul. 1, 2008.]

Raw material	Rigid	Semi-rigid	Flexible
PVC	100	100	100
DOP		20	44
Impact modifier (MBS, Paraloid BTA II N 2)	5		
Acrylic process aid (Paraloid K 120 N)	0.5		
Acrylic process aid (Paraloid K 175)	0.5		
Montan wax (Wax E)	0.3		
Lubricant (partial ester of glycerol, Loxiol G 16)	1.0		
Lubricant (pentaerythritol adipate, Loxiol G 71 S)			0.3
Calcium stearate			0.2
Epoxidized soybean oil	3.0	3.0	6.0
Nonylphenyl phosphite (Mark CH 302)			0.6
30% aqueous sodium perchlorate solution	0.6	0.2	0.04
Alkanolamine ($[CH_2N(CH_2CH_2OH)_2]_2$	0.4		
Alkanolamine ($N(CH_2CH_2OH)_3$)		0.5	
Alkanolamine (oleyl-$N(CH_2CH_2OH)_2$)			0.6
Initial yellowness index (without stabilizer 40.17)	9.49	6.03	8.48

Yellowness index was determined after 5 min rolling at 180°C. The above-selected system also provided long-term stability.

Efficient stabilizing systems. [Data from Hopfmann, T.; Friedrich, H.-H.; Kuhn, K.-J.; Wehner, W., **US Patent 7,358,286**, Apr. 15, 2008.]

Raw material	Rigid	Semi-rigid	Flexible
PVC (rigid: Evipol SH 5730, rest Evipol SH 7020)	100	100	100
DOP		20	47
Impact modifier (MBS, Paraloid BTA III/N2)	5		
Acrylate process aid (Paraloid K 120N)	0.5		
Acrylate process aid (Paraloid K 175)	0.5		
Montan wax (E wax)	0.3		
Lubricant (partial ester of glycerol of fatty acid, Loxiol G 16)	1		
Lubricant (multicomponent ester, Loxiol G 71 S)			0.3
Oxidized polyethylene wax (AC 629 A)		0.2	
Calcium stearate			0.1
Epoxidized soybean oil	3	3	3
30% solution in water of sodium perchlorate	0.6	0.2	0.5
Triethanolamine	0.2		
Diethanolsoyamine		0.2	
Triisopropanolamine			0.2
1,3-dimethyl-4-aminouracil	0.2	0.1	0.2
Phosphite (Mark CH 300)	0.5		
Initial yellowness index (5 min milling at 180°C)	11.6	9.1	9.6
Transparency, %	92.6	98.1	97.6

Improved weathering resistance. [Data from Hawrylko, R. B.; Krause, P. W.; Levesque, M., **US Patent 7,238,739**, Jul. 3, 2007.]

Raw material	Concentration, parts
PVC (Se 950 EG)	100
Dibutyltin ethyl hexyl mercaptoacetate (Thermolite T-31)	1
Zinc octoate (Baerostab L230)	0.5
Calcium stearate	1.25
Lubricant (mixture of fatty acid/alcohols, Loxiol G33)	0.25
Paraffin wax (Paraffin 165F)	0.65
Ethylene-bis-stearamide (EBS wax powder)	0.5

Improved weathering resistance. [Data from Hawrylko, R. B.; Krause, P. W.; Levesque, M., **US Patent 7,238,739**, Jul. 3, 2007.]

Raw material	Concentration, parts
Acrylic process aid (Paraloid K120N)	1
Titanium dioxide (Kronos 2160)	10
Acrylic lubricant/process aid (Paraloid K175)	1
Calcium carbonate (Optifil T)	12

Addition of Optifil T has been credited with improvement of weather stability.

Hydrotalcite. [Data from Eisgruber, M.; Ladebecki, J.; Koy, J.; Shiessling, H.; Buckl, W.; Ebert, H., **US Patent 7,211,235**, May 1, 2007.]

Raw material	Concentration, parts
PVC (Solvin 271 PC)	2
DIDP	1
Zinc stearate	0.1
Calcium stearate	0.2
Hydrotalcite	0.067

Natural hydrotalcite is derived from mineral brucite having the following formula: $[Mg_6Al_2(OH)_{16}]CO_3.nH_2O$. Hydrotalcite can also be obtained by synthesis, but consistency and quality were always problematic. This invention addresses cost-efficient production of hydrotalcite from inexpensive raw materials. A process is described in detail which leads to a production of hydrotalcite which has good performance as an acid scavenger in PVC formulations.

Ammonium chloride as PVC costabilizer. [Data from Beekman, G. F.; Conroy, G. M.; Hyde, J. R.; Norris, G. K., **US Patent 5,532,303**, Jul. 2, 1996.]

Raw material	Concentration, parts
PVC (Oxy 190)	100
Process aid (Acryloid K120N)	1.5
Impact modifier (Kane Ace B-22)	6
Oxidized polyethylene	0.2
Ester wax lubricant	1.7
Epoxidized soybean oil	1
Dimethyltin bis-(isooctyl thioglycolate) (Advastab TM-181)	1
NH_4Cl (solid)	0.1

Aluminum chloride is produced during synthesis of tin mercaptide thermal stabilizers. It was always believed that the ammonium chloride has to be removed from stabilizer because otherwise, its performance will suffer. This invention has shown that some quantities can be left in the stabilizing composition giving some benefits for stabilizing performance.

Calcium pyroborate as a microbiocide. [Data from Koshkiniemi, M. S., **US Patent 5,482,989**, Jan. 9, 1996.]

Raw material	Concentration, parts
PVC	100
DOP	40
Microbiocide	2

Calcium pyroborate was compared with barium metaborate (Busan 11M1), and a control containing 2 parts of talc filler. Calcium metaborate obtained a rating of 9 in mold growth testing, barium metaborate rating of 10 (both are no growth), and control rating of 5 which indicated medium to high growth. In fungi testing there was less than 10% growth area in the case of calcium metaborate compared with 30-60% growth area for barium metaborate, meaning that calcium metaborate is more effective against fungi than barium metaborate.

White oil extrusion lubricant. [Data from Cohen, S. C., **US Patent 6,663,931**, Dec. 16, 2003.]

Raw material	Concentration, parts
PVC	100
Stabilizer	0.3-1
External lubricant (paraffin wax)	0.6-1.5
Internal lubricant (calcium stearate)	0.4-1.5
Impact modifier (polyethylene wax)	0-0.3
Titanium dioxide	0.5-3
Filler (calcium carbonate)	0-5
Process aid/modifier	0-3
Hydrobrite PVC oil	1.45

The oil acts as an external lubricant. It is suggested as a lubricant for extruded products with special mention of production of potable water pipe, but it is also useful in the production of siding, window profiles, fences, doors, etc.

Gloss control of extrudate. [Data from Pickett, T. J.; Wenzel, E. J.; Franck, D. L.; Kratzer, J. P., **US Patent 5,264,164**, Nov. 23, 1993.]

It was discovered by the authors of this invention that gloss has an almost linear relationship with the temperature of the extrudate surface. Both temperature and length of the auxiliary die contribute to the gloss of the final extrudate. In their experiment, they used a 2.5-inch long die, and the temperature of the die increased by 25%, which produced 80 gloss readings. It was found that between 177 and 210°C, gloss could be controlled in the range between 40 and 100. Further increase in temperature causes burning.

Oxidized polyethylene as PVC lubricant. [Data from Schuster, L., Hettche, A.; Liedy, W.; Weiss, S.; Ehemann, L., **US Patent 5,064,908**, Nov. 12, 1991.]

Raw material	Concentration, parts
PVC (Vinoflex S 6115)	100
Organic tin stabilizer	1.2
Polyethylene oxidate	0.3

Polyethylene was oxidized for 0.5 to 2 hours in oxygen, air, or ozone at elevated temperature (125-128°C).

UV light stabilized PVC. [Data from Wallen, J. M., **US Patent 5,030,676**, Jul. 9, 1991.]

Raw material	Concentration, parts
PVC	100
Methyltin mercaptide (Mark 2212)	1
Calcium stearate	2.0
Paraffin wax (Hostalub XL 165STS)	0.95
Impact modifier (Acryloid KM-323B)	7
Process aid (Acryloid K-125)	0.7
Process aid (Acryloid K-175)	0.5
Titanium dioxide (R-69)	10
Magnesium oxide	0.5

Smoke suppressant. [Data from Batdorf, V. H., **US Patent 4,965,309**, Oct. 23, 1990.]

Raw material	Concentration, parts
PVC	95
Organotin heat stabilizer	1.7
Impact modifier (Wacker K-550)	10
Process aid (K-120ND)	2
Lubricant (Loxial G-71)	0.5
Lubricant (Loxial G-30)	0.2
Epoxidized soybean oil	1
Titanium dioxide	10
Paraffin wax (XL 165)	2.5
Hydrated alumina	39
Wollastonite (Nyad 475)	6.9
Zinc oxide (Kadox 15)	0.82
Zinc stearate	0.08
Zinc pyrophosphate	0.08
Magnesium hydroxide (particle size 1.7-2.4 μm)	1.7
Molybdenum trioxide (particle size 2 μm)	0.47

The above formulation produced about 3 times less smoke than control, which did not have the last 6 components. Zinc carbonate and magnesium carbonate were also tried with positive results as a replacement for zinc pyrophosphate and magnesium hydroxide.

4.5.2 BLINDS

4.5.2.1 Formulation found in the open literature

Vertical blinds. [Data from Rapacki, S. R., *J. Vinyl Additive Technol.*, **4**, 1, 12-21, 1998.]

Raw material	Concentration, parts
PVC (K=60)	100
Tin stabilizer	2
Calcium stearate	1
Paraffin wax	0.5
E-wax	0.6
Titanium dioxide	8
Calcium carbonate	5
Acrylic impact modifier	6
Process aid	1
Lubricating process aid	0.5

4.5.2.2 Patented invention

Textured Venetian blinds. [Data from Chen, C.-T., **US Patent 5,102,598**, Apr. 7, 1992.]

Raw material	Concentration, parts
PVC	100
Titanium dioxide	4
Plasticizer	2
Tribasic lead sulfate (to be replaced)	1.4
Stearic acid	0.2
Staple fibers (mixture of cotton, wool, and flax)	1-2

Fenestration product. [Data from Melkonian, G, **World Patent WO2011062632**, May 26, 2011, *Mikron Industries, Inc.*]

Raw materials	Concentration, parts
PVC (Shintech SE-650)	100
Tin butyl stabilizer (Reagens RT4458)	1.2
Ester-base lubricant (Structol SA 0817B)	1.5
Acrylic modifier (Kaneka PA 40)	20
$CaCO_3$ (JM Huber Optifil JS-JM)	6
Pigment (KibbeChem 473LD)	5

4.5.3 CLEAR COMPOUND

4.5.3.1 Formulation proposed by the raw material supplier

Clear extruded compound. [Data from **Mark 1921**. Technical data sheet. *Crompton*.]

Raw material	Concentration, parts
PVC (medium molecular weight)	100
MBS impact modifier	10
Ester wax	0.5
Mark 1921 (methyltin mercaptide)	2
Acrylic process aid	2

4.5.4 FENCING AND DECKING

4.5.4.1 Formulation found in the open literature

Fencing. [Data from Wiebking, H. E., *J. Vinyl Additive Technol.*, **12**, 1, 37-40, 2006.]

Raw material	Concentration, parts
PVC resin (K=66)	100
Stabilizer (methyltin)	1.25
Process aid (acrylic)	1.00
Calcium stearate	1.00
Paraffin wax	1.25
PE wax	0.15
Acrylic impact modifier	10
Precipitated calcium carbonate (0.35 μm, Tuffgard)	10
Talc (average particle size = 0.9 μm, UltraTalc 609)	15-20

The addition of talc increases the flexural modulus at elevated temperature, which leads to improved dimensional stability. Use of high concentration of ultrafine talc with precipitated calcium carbonate and acrylic impact modifier also permits an increase of dimensional stability and high impact strength.

4.5.5 FOAMED PROFILES

4.5.5.1 Formulation proposed by the raw material supplier

Foamed PVC profile. [Data from Ettore Nanni, **PVC Stabilizers**, *Reagens*, 2013.]

Raw material	Concentration, parts
PVC	100
$CaCO_3$	6
TiO_2	3
Acrylic processing aid	8
Flame retardant	1.5
ESBO	1
Calcium-based stabilizer	4.6
Foaming agent	0.7

4.5.6 GASKETS

4.5.6.1 Formulation proposed by the raw material supplier

Refrigerator gasket. [Data from **Dow Hyperlast**. Dioplex 917. *DowDuPont*, 2004.]

Raw material	Concentration, parts
PVC (K=65)	100
Dioplex 917	80
Epoxy plasticizer	8
Calcium stearate	3
Filler	20

Refrigerator gasket. [Data from **Mark 3070**. Technical data sheet. *Crompton*.]

Raw material	Concentration, parts
PVC	100
Drapex P-1 (polymeric plasticizer)	60-70
Drapex 6.8	10-20
Calcium carbonate	20-60
Stearic acid	0-0.2
Titanium dioxide	0.5-1.5
Mark 3070 (non-toxic zinc stabilizer)	0.75-1

4.5.6.2 Patented inventions

Magnetic door gasket [Data from **CN102936384B**, Feb. 25, 2015.]

Raw material	Concentration, parts
PVC	75
Chlorinated PVC	25
Environmentally-friendly plasticizer	38
Magnetic powder	55
Thermal stabilizer	3.5
$CaCO_3$	15
Pigment	2.5

High temperature gasket material [Data from **CN103524928B**, May 4, 2016.]

Raw material	Concentration, parts
PVC	70
DOTP	30
Ca/Zn stabilizer	0.5

Pasteurization is used to kill bacteria while preserving the flavor articles nutrients of soy milk. The soy milk is heated to 125°C and incubated for 25-30 minutes. A conventional PVC begins to soften at 80-85°C, and cannot withstand 125°C. The gasket manufactured according to the above formulation withstands up to 135°C.

4.5.7 INTERIOR AND EXTERIOR PROFILES

4.5.7.1 Formulation found in the open literature

Interior profile formulation for single and twin extruders. [Data from Rapacki, S. R., *J. Vinyl Additive Technol.*, **4**, 1, 12-21, 1998.]

Raw material	Single	Twin
	Concentration, parts	
PVC (K=66)	100	100
Tin stabilizer	2	1.5
Calcium stearate	0.8	0.8
Paraffin wax	0.75	1
Calcium carbonate	5	5
MBS impact modifier	8	8
Process aid	1	1
Lubricating process aid	1	1

Profiles for detection of neutrino. [Data from Grudzinski, J. J.; Talaga, R. L.; Pla-Dalmau, A.; Fagan, J. E.; Grozis, C.; Kephart, K.; Fischer, R.; *J. Vinyl Addit. Technol.*, **22**, 368-76, 2016.]

Ingredient	Commercial name	Content, parts
PVC	Shintech SE950EG (high reflectivity)	100
Tin stabilizer	Advastab TM-181 (20% monoethyl tin)	2.5
Titanium dioxide anatase	Kronos 1000	19
Calcium stearate	Ferro 15F	0.8
Paraffin wax	Ferro 1654	1.1
Oxidized polyethylene	Ferro Petrac 215	0.2
Glycerol monostearate	F1005 Rohm & Haas	0.3
Acrylic impact modifier	Durastrength 200 Arkema	4
Processing aid	Paraloid K120N	1

14,000 ton self-supporting structure was build to detect neutrinos. The primary parts in the detector construction were 15.5 m long, 16-cell PVC extruded profiles of unique characteristics. Because of the method of detecting neutrinos, the profiles had to possess exceptionally high reflectivity over a particular wavelength range. This requirement placed restrictions on the components of the PVC formulation which was selected after 2 years of experimentation.

4.5.7.2 Patented inventions

Whitening-free, weather-resistant PVC extrusion profile [Data from **CN105385067A**, Mar. 9, 2016.]

Raw material	Concentration, parts
PVC, polymerization degree 800	100
Impact modifier (methacrylate-based)	4.5
Ca/Zn stabilizer	3
Aliphatic pentaerythritol stearate lubricant	0.7
Paraffin wax	0.7
Stearate and oxidized PE wax mixture	0.6
Tris (2,4-di-t-butylphenol) phosphite	0.35
Benzotriazole-type UV absorber	0.2
Pigment	0.35

4.5.8 PANELS

4.5.8.1 Technology proposed by raw material supplier

Nidacell is a technology protected by several groups of Solvay patents. It is capable of production of 3D objects such as panels from a range of polymers including soft, rigid, and recycled PVC. Panels produced by this technology can be used in building construction, furniture, sport, and leisure. Honeycomb structures produced in the process are light, rigid, and relatively inexpensive. More information about the technology can be found elsewhere (http://www.solvayplastics.com/sites/solvayplastics/EN/vinyls/Pages/Nidacell.aspx).

4.5.8.2 Patented inventions

Panel protecting rear of solar panels. [Data from Bizet, S, Bonnet, A, Devisme, S, Ramfel, B, World Patent **WO2012146880**, Nov. 1, 2012, *Arkema France.*]

Raw material	Concentration, wt%
Lacovyl GB 1040	71.1
$CaCO_3$ (Micromya)	7.9
Kane Ace B 382	2.1
Plastistrength 770	0.7
Internal lubricant	1.1
External lubricant	0.3
Ca/Zn stabilizer	3.9
TiO_2 (Kronos 2220)	2.6
Glass fiber	10.3

PVC/wood panel. [Data from Fest, D E, Das, K, **Canadian Patent CA2660969**, Sep. 30, 2010, *Alside Materials, Llc.*]

Raw material	Concentration, parts
PVC	100
Wood flour	166
Thermal stabilizer	1.2
Process aid	6
Impact modifier	2
Wood stabilizer	1
Lubricating process aid	2
Lubricant	14
Calcium carbonate	75
Calcium stearate	1.5
Foaming agent	1.5

4.5.9 PIPES

4.5.9.1 Formulations proposed by the raw material suppliers

Ca/Zn pipe formulation. [Data from **Waxes for PVC Lubrication**. *Clariant*, 2013.]

Raw material	Concentration, parts
S-PVC (K=65-68)	100
Ca/Zn stabilizer	2.2
Phosphite (TNPP)	0.4
PMMA impact modifier	1
Distearyl phthalate	0.4
Hydroxystearic acid	0.2
Licocene PE 4201/Licocene PP 6102/Licolub H4	0.5
Licowax PE 520	0.2

Sn pipe formulation (twin screw). [Data from **Waxes for PVC Lubrication**. *Clariant*, 2013.]

Raw material	Concentration
S-PVC (K=65-68)	100
Sn stabilizer containing sulfur	0.4
Calcium stearate	0.8
MBS impact modifier	1
Licocene PE 4201/Licocene PP 6102/Licolub H 4	0.7-1.2
Licolub H 12	0.2
TiO_2	1
$CaCO_3$	5

Pipe formulations. [Data from **Thermolite 176, 176C and 178**. *Arkema*.]

Raw material	Potable water	PVC conduit	Sewer pipe
	Concentration, parts		
PVC (K=65)	100	100	100
Thermolite 178	0.35	0.5	
Thermolite 176 or 176C			0.3-0.5
Calcium stearate	0.4-0.8	0.8	0.6-0.8
Paraffin wax (melting point=75°C)	0.8-1	1.10	1.2-1.5

Pipe formulations. [Data from **Thermolite 176, 176C and 178**. *Arkema*.]

Raw material	Potable water	PVC conduit	Sewer pipe
	Concentration, parts		
Oxidized PE wax	0.1-0.2	0.15	0.1-0.2
Calcium carbonate (0.8 μm)	2-4	10-20	10-30
Titanium dioxide	1-2		0.75-1
Durastrength 200		2-3	2

Pipe products. [Data from **Advastab TM-694**. *Rohm & Haas*. April 2002.]

Raw material	pressure	sewer	duct	foam/skin
	Concentration, parts			
PVC (K=66)	100	100	100	100
Titanium dioxide	0.5-1	0.5-1	0.5-1	0.75-1
Calcium carbonate	3-5	15-30	2.4-4	3-5
Calcium stearate	0.6	0.6	0.8	0.6
Paraffin (MP=74°C)	1.2	1.2	1.2	1.2
Oxidized polyethylene	0.15	0.2	0.15	0.15
Paraloid KM-399			2-5	0-3
Advastab TM-694 (reverse methyltin ester)	0.3-0.4	0.3-0.4	0.35-0.45	0.3-0.4

NSF (National Sanitation Foundation)/PPI pipe. [Data from **Mark 2910**. Technical data sheet. *Crompton*.]

Raw material	Concentration, parts
PVC	100
Titanium dioxide	1
Calcium carbonate	5
Calcium stearate	0.6-0.8
Oxidized polyethylene wax	0.15
Mark 2910 (methyltin stabilizer/external lubricant)	1.75-2.25

Application of Mark 2910 eliminates the need for paraffin wax in the pipe formulation.

Pressure pipe, type I. [Data from **Mark 1900**, Technical Data Sheet, *Crompton*]

Raw material	Single screw	Twin screw
	Concentration, parts	
PVC medium to high molecular weight	100	100
Acrylic process aid	2-2.5	0-1.5
MarkPet or Sunolite 160 (external/internal lubricant)	0.5-1	11-1.5
Calcium stearate	1-2	0.5-0.8
Polyethylene (low molecular weight)		0.1-0.4
Titanium dioxide	1-2	1-2
Mark 1900 (organotin, mercaptide type, stabilizer)	0.8-1.5	0.3-0.5

Pipe (foam core). [Data from **Celogen AZRV**. Chemical foaming agent. *Crompton*.]

Raw material	Concentration, parts
PVC (K=67)	100
Tin stabilizer	0.8
Calcium stearate	0.7
Paraffin wax 165	1.3
Titanium dioxide	1
Calcium carbonate	5
Paraloid K175	0-0.5
Paraloid K400	3
Celogen AZRV (modified azodicarbonamide)	0.3-0.6

4.5.9.2 Formulations found in the open literature

Pipe – starting formulation. [Data from Carroll, W. F., Johnson, R. W., Moore, S. S., Paradis, R. A., **Applied Plastics Engineering Handbook**, Chapter 5. Poly(vinyl chloride), *Elsevier*, 2011, p. 61-76.]

Raw material	Concentration, parts
PVC (K=65-67)	100
Stabilizer	low tin
Filler	0-5
TiO_2	0.5-1
Processing aid	0-1

Pipe – starting formulation. [Data from Carroll, W. F., Johnson, R. W., Moore, S. S., Paradis, R. A., **Applied Plastics Engineering Handbook**, Chapter 5. Poly(vinyl chloride), *Elsevier*, 2011, p. 61-76.]

Raw material	Concentration, parts
Calcium stearate	0.5-0.9
Paraffin wax	0.8-1.5
Oxidized polyethylene	0.1-0.3

Drain waste & vent, DWV, pipe. [Data from Rapacki, S. R., *J. Vinyl Additive Technol.*, **4**, 1, 12-21, 1998.]

Raw material	Concentration, parts
PVC (K=67)	100
Tin stabilizer	0.4
Calcium stearate	0.6
Paraffin wax	1.2
Polyethylene wax	0.15
Titanium dioxide	1
Calcium carbonate	30
Lubricating process aid	0.75

Drainage pipe with organic-based stabilizer, OBS 200 series. [Data from Edser, C., *Plastics Additives Compounding*, **3**, 11, 26-30, 2001.]

Raw material	Concentration, parts
PVC (suspension, K=67)	100
OBS 200 series	2.0-2.5
Impact modifier	0-5
Costabilizer (epoxidized soybean oil)	0-1
Filler	5-10
Pigment	quantum satis

Pipe containing lead stabilizers. [Data from Fujiyama, M.; Kondou, M., *J. Appl. Polym. Sci.*, **90**, 7, 1808-1824, 2003.]

Raw material	Concentration, parts
PVC	100
Monohydrous tribasic lead sulfate	1.5
Lead stearate	1
Stearic acid	0.2
Calcium stearate	0.2
Acrylic process aid	0.5

This process is sensitive to melt fracture and die swell, and both have to be well controlled to obtain a quality product.

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Irrigation pipe. [Data from Rapacki, S. R., *J. Vinyl Additive Technol.*, **4**, 1, 12-21, 1998.]

Raw material	Concentration, parts
PVC (K=67)	100
Tin stabilizer	0.4
Calcium stearate	0.8
Paraffin wax	1.2
Polyethylene wax	0.15
Titanium dioxide	8
Calcium carbonate	5
Acrylic impact modifier	3
Process aid	0.75

Potable water pipe. [Data from Rapacki, S. R., *J. Vinyl Additive Technol.*, **4**, 1, 12-21, 1998.]

Raw material	Concentration, parts
PVC (K=67)	100
Tin stabilizer	0.4
Calcium stearate	0.8
Paraffin wax	1.2
Polyethylene wax	0.15
Titanium dioxide	1
Calcium carbonate	3
Process aid	0.75

Pressure pipe with organic-based stabilizer, OBS 200 series. [Data from Edser, C., *Plastics Additives Compounding*, **3**, 11, 26-30, 2001.]

Raw material	Concentration, phr
PVC (suspension, K=67-68))	100
OBS 200 series	2
Calcium carbonate	0-5
Pigment	quantum satis

Many benefits are associated with the use of an organic-based stabilizer. They include an environmentally friendly nature (no heavy metals, approved for direct contact with food, suitable for drinking water application), outstanding performance (process stability, suppressed crosslinking, wide processing window, no problems with light colored systems), and odor-free.

Rain gutter pipe with organic-based stabilizer, OBS 200 series. [Data from Edser, C., *Plastics Additives Compounding*, **3**, 11, 26-30, 2001.]

Raw material	Concentration, parts
PVC (suspension, K=64-67)	100
OBS 200 series	2.0-2.3
Process aid	0-1
Impact modifier	0-1
Costabilizer (epoxidized soybean oil)	0-1
Filler	5-15
Pigment	quantum satis

Sewage pipe with organic-based stabilizer, OBS 200 series. [Data from Edser, C., *Plastics Additives Compounding*, **3**, 11, 26-30, 2001.]

Raw material	Concentration, parts
PVC (suspension, K=67-68)	100
OBS 200 series	2.0-2.2
Filler	5-20
Pigment	quantum satis

Telephone duct. [Data from Rapacki, S. R., *J. Vinyl Additive Technol.*, **4**, 1, 12-21, 1998.]

Raw material	Concentration, parts
PVC (K=67)	100
Tin stabilizer	0.4
Calcium stearate	0.8
Paraffin wax	1.2
Polyethylene wax	0.1
Titanium dioxide	0.5
Calcium carbonate	20
Acrylic impact modifier	2
Lubricating process aid	0.75
Carbon black	0.05

4.5.9.3 Patented inventions

Pipes and accessories for home and industrial use. [Data from Table, O. P.; Estrada, L. V.; Sanchez, A. P., **US Patent 7,423,081**, Sep. 9, 2008.]

Raw materials	Invention	Commercial product
	Concentration, parts	
CPVC (K=58-67)	100	
Antioxidant	0.75	
Melt promoter	1.5	
Thermal stabilizer (methyltin mercaptide)	3	
Impact modifier (MBS)	10	
Polyethylene wax	1.35	
Oxidized polyethylene wax	0.3	
Stearic acid+fatty acid waxes	0.25	
Oxidized ethylene homopolymer	0.73	
Paraffinic wax	2.2	
Tensile strength, MPa	66.34	50.8
Elasticity modulus, MPa	2627	2551
Izod impact, J/m	555	374
Heat distortion temperature, °C	110	111
Stable torque, N-m	26	34
Stable torque temperature, °C	210	213
Fusion time, min	1.5	1

Pipes and accessories for home and industrial use. [Data from Table, O. P.; Estrada, L. V.; Sanchez, A. P., **US Patent 7,423,081**, Sep. 9, 2008.]

Raw materials	Invention	Commercial product
	Concentration, parts	
Dynamic thermal stability, min	18	12
Melt index, g/10 min	4.34	0.87

Flame retardant pipe. [Data from Zucchelli, U, **World Patent WO2014013284**, Jan. 13, 2014, *Italmatch Chemicals SPA*.]

Raw material	Concentration, parts
PVC (K=70)	100
Palatinol DOP	50
Repak G-NT/7526 (stabilizer)	3
Reaflex EP/6 (costabilizer)	5
Phoslite IP-A (flame retardant)	3

High-output dry blend for PVC pipe manufacture. [Data from Mundra, M K, **World Patent WO2013048775**, Apr. 4, 2013, *Dow Global Technologies*.]

Raw material	Concentrations, wt%
PVC (Oxyvinyl 240F)	44.23
$CaCO_3$ (Hubercarb Q1T)	30.08
LPLAS-1101 (mixture of Soy-eFAME:ESO bio-based plasticizer from DOW) + Irganox 12076	23.16+1.2
Baeropan 9754KA (heat stabilizer)	1.33

The bio-based plasticizer is environmentally friendly and derived from renewable resources (see **US Patent US20100010127** to find details about this plasticizer). The PVC dry blend compositions prepared according to the process of the invention provide improved output feed rates as compared to the output feed rates of a PVC dry blend prepared from conventional phthalate. PVC and stabilizer are first mixed and heated to stock temperature. Plasticizer preheated to 60°C is pumped into PVC stock mixture, then filler is added and mixture compounded until discharge temperature is reached.

Double wall pipe. [Data from Drossbach, H. M., **US Patent 5,124,109**, Jun. 23, 1992.]

Raw material	Concentration, wt%
PVC	90.58
Calcium carbonate	2.717
Acrylic process aid	1.812
Chlorinated polyethylene	1.359
Paraffin wax	1.268
Titanium dioxide	0.906
Calcium stearate	0.453
Carbon black pigment	0.362
Antimony oxide	0.362
Polyethylene wax	0.181

Extruded heat shrink protective seamless PVC piling sleeve [Data from McCartney, S.; Porter, M., **US20160089846A1**, *Shoreline Plastic, LLC*, Mar. 31, 2016.]

Raw material	Concentration, wt%
PVC 100	100
UV inhibitor	4
Calcium carbonate	5
Calcium stearate	0.8
Paraffin wax	1.2
Oxidized polyethylene	0.2
Plasticizer	7
Marine growth inhibitor	0.02
Heat stabilizer	1.2
Process aid	4
Gray color	1.75
Epoxidized soybean oil	3
UV absorber	1

Rigid PVC pipe with excellent stiffness and resistance to water pressure [Data from **WO2015016491A1**, Feb. 5, 2015.]

Raw material	Concentration, wt%
PVC K=72	100
Tin stabilizer	2.5
Acrylic impact modifier (butyl methacrylate:methyl methacrylate=1:1)	4
Lubricant	4

Extruded microcellular foam pipe [Data from Overeijnder, H.; Schuurman, J., **EP2990435A1**, *Wavin BV*, Mar. 2, 2016.]

Raw material	Concentration, wt%
PVC K=67	100
Lead based stabilizer	q.s.
Omyalite 50H	18
Foaming gas nitrogen	0.04 wt%

Poly(vinyl chloride) pipe [Data from Petr, M. T.; Rapacki, S. R., **WO2017184709A1**, *Rohm and Haas Company*, Oct. 26, 2017.]

Raw material	Concentration, parts
PVC K=66	100
Calcium stearate	0.6
Heat stabilizer (AdvastabTM-694)	0.85
Lubricant (AC-629)	0.3
TiO_2	0.6
$CaCO_3$	5
Paraffin wax (XL-165)	1.4

Pipe composition [Data from Smith, M. A.; Marti, T.; St. Onge, B; St. Onge, H, **US8796407B2**, *Underground Solutions Technologies Group Inc*, Aug. 5, 2014.]

Raw material	Concentration, parts
PVC	100
Lubricant combination of calcium stearate, paraffin wax and polyethylene wax	2
Titanium dioxide	3
Calcium carbonate	2
Processing aid, Rohm & Haas K120N	1
Blue colorant	0.2
Heat stabilizer	0.8

Calcium carbonate filler and formula for pipe production. [Data from Blanchard, P, **World Patent WO2013120934**, Aug. 22, 2013, *Omya Development AG*.]

Raw material	Concentration, parts
PVC (Evipol SH6630)	100
Ca/Zn stabilizer (Stabilox CZ 2913 GN)	4.3
Lubricant 12-hydroxy stearic acid (Realube AIS)	0.2
Lubricant polyethylene wax (Realube 3010)	0.15
Titanium dioxide (Kronos 2220)	3.5
Acrylic impact modifier (Durastrength 340)	6
Ground natural $CaCO_3$ (invention)	8-16

The calcium carbonate of the invention is an untreated product having a particle size of 0.8 μm and BET surface area of 7-8 m^2/g. The filler has excellent dispersing properties.

Irrigation pipe. [Data from Dorn, C., **US Patent 4,577,998**, Mar. 25, 1986.]

Raw material	Concentration, parts
PVC (K=67, Corvic S67/111)	100
Tribasic lead sulfate (getting obsolete now)	5
Diisooctyl phthalate	50
Calcium stearate	1
Acrylic process aid (Diakon APA 1)	5

Irrigation pipe. [Data from Dorn, C., **US Patent 4,577,998**, Mar. 25, 1986.]

Raw material	Concentration, parts
Azodicarbonamide (Genitron EPA)	1
Blowing agent (p,p'oxy-bis(benzenesulfonylhydrazide))	1
Titanium dioxide (pigment)	0.5
Carbon black (pigment)	0.02

4.5.10 PLANKS

4.5.10.1 Patented inventions

Thermoplastic planks. [Data from Chen, H. A.; Judd, R., **US Patent 7,419,717**, Sep. 2, 2008.]

Raw material	Concentration, parts
PVC (Geon X150-206-050-02)	100
Thermal stabilizer	0.8-1.5
Process aid	0.5-1.0
Impact modifier	3-4
Internal lubricant	0.6-1
External lubricant	1.1-1.5
Filler	20-35
Titanium dioxide	1.5-3

The product proposed in this invention is designed to replace laminate flooring composed of medium density fireboard or particle board and PVC laminate. The weakness of this flooring method is its moisture resistance (particularly moisture resistance of particle board). This product of the invention may have three layers (core layer (as given by formulation in the table above), print layer, and wear layer).

Thermoplastic laminate plank. [Data from Chen, H A, Judd, R, **US Patent US20160052245A1**, *Valinge Innovation AB*, Feb. 25, 2016.]

Raw material	Concentration, parts
Extrusion grade PVC	100
Tin mercaptide stabilizer	2-4
Acrylic processing aid	1-3
Filler	10-30
Impact modifier (acrylic)	3-10
Lubricant package	2-5
Pigment	1-5

Wood composite with improved mechanical properties. [Data from Bacaloglu, R.; Kleinlauth, P.; Frenkel, P., **US Patent 7,390,846**, Jun. 24, 2008.]

Raw material	Concentration, parts
PVC (Oxy 185F)	100
Wood flour	40
Acrylic impact modifiers (PA 40 and PA 101)	6
Chlorinated polyethylene wax impact modifier (CPE-3615P)	5
Calcium stearate	0.6
Paraffin wax and Marklube L-106	1.3
Lubricant (oxidized polyethylene; AC 629A)	0.2
Zinc stearate	0.6
Wood sizing stabilizer (sodium salt of polymethacrylic acid (MW=6500))	2

Extrudable thermoplastic with capstock layer. [Data from Jeng, J P, **US Patent US20100330272**, Dec. 30, 2010, *Certainteed Corporation*.]

Raw material	Concentration, parts
PVC	100
Methyltin stabilizer	1
Calcium stearate	1.4
Polyethylene wax	0.2-0.3
Paraffin wax	1.5
Acrylic impact modifier	4
TiO_2	0.8
$CaCO_3$	10

Building material and method of its manufacture is included in the invention. The product consists of an extrudable thermoplastic (e.g., PVC of the above formulation) or thermosetting substrate having a fluorocarbon-based capstock layer applied to the substrate. The fluorocarbon-based capstock layer can further include one or more top coats for providing a variegated, colored or textured pattern. The capstock layer has a thickness of less than 4 mil and contains a UV-resistant PVDF resin.

Non-staining wood composite. [Data from Ruede, P., **US Patent 7,291,661**, Nov. 6, 2007.]

Raw material	Concentration, parts
PVC regrind (5-8 wt% of calcium carbonate)	62
Oak flour	38
Succinic anhydride	0.6

Wood tannins from oak flour stain PVC composites containing calcium carbonate in the presence of moisture. Succinic anhydride is capable of preventing staining, providing its concentration is sufficient. The higher the content of calcium carbonate, the higher the concentration of succinic anhydride required.

4.5.11 RIGID ARTICLES

4.5.11.1 Formulations proposed by the raw material suppliers

White PVC profile. [Data from Ettore Nanni, **PVC Stabilizers**, *Reagens, PVC Formulations* 2013.]

Raw material	Concentration, parts
PVC K57	100
Coated filler	6
TiO_2	6
Acrylic impact modifier	3
CPE impact modifier	3
Processing aid	1
Calcium-based stabilizer	3.5

Rigid profile for outdoor use. [Data from **Mark 2289**. Technical data sheet. *Crompton*.]

Raw material	Concentration, parts
PVC (K=66)	100
Titanium dioxide (for outdoor use)	10
Paraffin wax	1
Impact modifier (for outdoor use)	10
Process aid	1
Lubricating process aid	1
Mark 2289 (sulfur-free organotin stabilizer for outdoor use)	4.35

Rigid profile. [Data from **Sorbacid 911. Hydrotalcite as costabilizer for PVC**. *Sued-Chemie AG*.]

Raw material	Concentration, parts
PVC (K-68)	100
Impact modifier	7
Process aid	1
Titanium dioxide	4
Filler	6
Ca/Zn stabilizer	2.2
Sorbacid 911 (hydrotalcite)	0.8

Time to HCl emission was increased by the addition of hydrotalcite from 21 to 25 min.

Rigid PVC compound with Elvaloy. [Data from **DuPont Elvaloy**, *DuPont*, K-16359-1, 2009.]

Raw material	Concentration, parts
PVC	100
Impact modifier (Elvaloy HP661)	6
Tin stabilizer	1.3
Acrylic process aid	1
Calcium stearate	0.6
Paraffin wax	1.2
Glycerol monostearate	0.4
Oxidized polyethylene	0.2
Calcium carbonate	2
Titanium dioxide	9

Food-contact rigid PVC. [Data from **Mark 1500**. Technical data sheet. *Crompton*.]

Raw material	Concentration, parts
PVC	100
Drapex 6.8 or 10.4	1-3
Mark QED (Ca/Zn stabilizer)	0.5-1.2
Mark 1500*	0.5-1

Food-contact rigid PVC. [Data from **Mark 1500**. Technical data sheet. *Crompton*.]

Raw material	Concentration, parts
FDA-cleared impact modifier	0-15
FDA-cleared process aid	1-3
Hystrene 5016 (stearic acid)	0-1

*4,4'-isopropylidenediphenol alkyl (C12-C15) phosphite (FDA-cleared)

4.5.11.2 Formulation found in the open literature

Rigid articles. [Data from Effler, L. J.; Berard, M. T., *J. Vinyl Additive Technol.*, **9**, 1, 19-25, 2003.]

Raw material	Concentration, parts
PVC (K=68)	100
Tin stabilizer	1
Calcium stearate	0.75
Paraffin wax	1
Glycerol monostearate	0.5
Oxidized polyethylene	0.15
PMMA process aid	1
Calcium carbonate	2
Titanium dioxide	9
Chlorinated polyethylene (25 or 36)	5

Using CPE-25 opens new possibilities not available with CPE-36. It gives faster fusion and enhanced melt strength without reduction of impact strength and weathering performance.

4.5.11.3 Patented inventions

PVC profile with high content of mineral filler. [Data from Bussels, R, Gabriels, J P, Spijkerman, **World Patent WO2010049532**, May 6, 2010, *Tessenderlo Chemie*.]

Raw material	Concentration, parts
PVC (K=65)	100
CaZn stabilizer	3.5
Lubricant	1.9
Processing aid	8
Toughening agent	6
Talc	110

Extrudable profile containing wood flour. [Data from Cope, C. W., **US Patent 6,066,680**, May 23, 2000.]

Raw material	Solid	Foamed
	Concentration, parts	
PVC	100	100
Tin stabilizer (Mark 1924)	2	2
Acrylic process aid (Kaneka K12)	7	7
Filler (calcium carbonate)	4	4
Wood flour	15-60	15-60
Lubricant (calcium stearate)	1	1
Ester lubricant (Loxiol 187S)	1.5	1.5
Wax lubricant (oxidized polyethylene, AC-629A)	0.1	0.1
Blowing agent (Hughes HRVP 01)		0.2-0.7
Whitener (titanium dioxide)		0-10

Extrudable material containing cork. [Data from Mezzalira, A, Mascolo, R, **World Patent WO2011125008**, Oct. 13, 2011, *Fitt SPA*.]

Raw material	Concentration, wt%
PVC	50
DINP	30
Epoxidized soybean oil	1.75
Ca/Zn stabilizer	0.43
Cork granulate	13.62

Rigid PVC formulation. [Data from Eilers, K. L.; Kopacki, A. F., **US Patent 3,983,186**, Sep. 28, 1976.]

Raw material	Concentration, parts
PVC	100
Organotin mercaptide (Thermolite 31)	2
Calcium stearate	2
Polyethylene wax (PE-629)	0.1
Titanium dioxide	1
Methacrylate-butyl acrylate process aid of this invention	1

4.5.12 SHEET

4.5.12.1 Formulation proposed by the raw material supplier

Outdoor and clear sheet. [Data from **Thermolite 108 and 109**. *Arkema*.]

Raw material	**outdoor**	**clear**
	Concentration, parts	
PVC (K=60)	100	100
Thermolite 108		0.8-1.7
Thermolite 109	1.2-1.5	
Internal lubricant	1.2-1.5	0.6-1
External lubricant	0.1-0.5	
Plastistrength 550	1.5-2	1-2
Plastistrength 710	0.7-1	
Plastistrength L-1000	0.1-0.4	
Clearstrength 303H	6-12	5-10
Toner	quantum satis	

4.5.12.2 Formulations found in the open literature

Thick sheet. [Data from Rapacki, S. R., *J. Vinyl Additive Technol.*, **4**, 1, 12-21, 1998.]

Raw material	**Concentration, parts**
PVC (K=66)	100
Tin stabilizer	2
Calcium stearate	2
Paraffin wax	0.7
Titanium dioxide	10
Calcium carbonate	3
Acrylic impact modifier	6
Medium-high molecular weight process aid	3
Lubricating process aid	0.5

PVC sheet stabilized with hydrotalcite. [Data from Gilbert, M, Ho, K C, Hitt, D J, Vrsaljko, D, *Polym. Deg. Stab.*, **98**, 1537-47, 2013.

Raw material	Concentration, parts
PVC (Evipol SH6830)	100
Naftosafe P WX 15860 (Ca/Zn soap stabilizer)	4
Hydrotalcite (Alcamizer P93 or Sorbacid 911)	2
Stearic acid	0.5

Nanocomposites based on organically modified montmorillonite with improved barrier properties. [Data from Petersen, H.; Jakubowicz, I.; Enebro, J.; Yarahmadi, N., *J. Appl. Polym. Sci.*, **135**, 42876, 2016.]

Raw material	Concentration, parts
Norvinyl S6045	100
Palatinol N (DINP)	15
Barostab 8807 14 (Ca/Zn)	1.5
Edenol D 81 (ESO)	1.5
Montmorillonite	5
Tributyl citrate	2.5

4.5.12.3 Patented inventions

Compostable PVC sheets and composites. [Data from Grossman, R. F., **US Patent 7,390,841**, Jun. 24, 2008.]

Raw material	Concentration, parts
PVC (Geon 121)	100
Dioctyl adipate	80
Dibutyltin laurate	2
Titanium neoalkanate, tridioctyl pyrophosphate-O-(adduct)-N substituted methacrylamide (Kenrich LICA 38J)	5

It was found that PVC can be made biodegradable, comparable to cellulosic polymers with the addition of prodegradant (LICA 38J). The above formulation is given as an example but can be modified to requirements because biodegradability is not affected by PVC additives.

PVC sheet stabilization. [Data from Berna, M, Gardi, S, Sarti, G, **European Patent EP2662403**, Nov. 13, 2013, *Reagens SPA*.]

Raw material	Concentration, parts
PVC (K=65)	100
Calcium carbonate (Omyalite 90 T)	5
Titanium dioxide (Kronos 2220)	1
Oxidized polyethylene wax (Cara tipo Hostalub H 12)	0.2
Calcium stearate	0.5
Tetrakis[methylene-3-(3',5'di-t-butyl-4'hydroxyphenyl)propionate]methane (Arenox A/1 0)	0.2
Zinc stearate	0.2
Hindered amine of polyalkylpiperidine type (Chimassorb 944)	0.2
Polyalkylpiperidine/zinc	9.22

Sheets for production of medical tools. [Data from Kimura, R.; Ishizuka, H.; Shibasaki, J., **US Patent 7,279,509**, Oct. 9, 2007.]

Raw material	Semi-rigid	Flexible
	Concentration, parts	
PVC	100	100
DOP	20	50
Epoxidized soybean oil	2	2
Calcium carbonate	10	
Zinc stearate	0.5	0.3
Calcium hydroxide	1	
Calcium stearate		0.2
Zinc pyrithione	0.01	0.01
Cyclic organic phosphoric ester compound	0.5	0.3

Glass fiber reinforced PVC. [Data from Budich, W.; Gasper, B.; Scharf, K.-G.; Wissinger, W., **US Patent 4,455,398**, Jun. 19, 1984.]

Raw material	Concentration, parts
S-PVC (K=64)	100
Stabilizer mixture	3
Glass fiber (length 6 mm, diameter 10 μm)	15
Calcium carbonate (average particle < 10 μm)	15
1,2-hydroxystearic acid	0.3
Oxidized polyethylene wax	0.5
Calcium stearate	0.5
Epoxidized soybean oil	1

Addition of glass fiber causes an increase in tensile strength by a factor of up to two. Modulus of elasticity, impact resistance, and heat deflection temperature can be improved by varying the proportions between the glass fiber and calcium carbonate.

A combination of zinc pyrithione and cyclic organic phosphoric ester compound renders antibacterial properties to medical tools produced, according to the invention.

4.5.13 SIDING

4.5.13.1 Formulations proposed by the raw material suppliers

Sn siding (twin screw extruder). [Data from **Waxes for PVC Lubrication**. *Clariant*, 2013.]

Raw material	Concentration, parts
S-PVC (K=67)	100
Sn stabilizer containing sulfur	1.2
MBS impact modifier	5
PMMA processing aid	0.5
Calcium stearate	1.2
Licocene PE 4201/Licocene PP 6201/Licolub H 4	1
Licolub H12	0.2
TiO_2	10

Vinyl siding. [Data from **Marklube L-126**. Technical data sheet. *Crompton*.]

Raw material	capstock	substrate
	Concentration, parts	
PVC	100	100
Mark 1900 (methyltin mercaptide)	1.2	
Mark 1971 (methyltin mercaptide)		1
Acrylic impact modifier	4.5	4.5
Acrylic process aid	0.5	0.5
Titanium dioxide	10	1
Calcium carbonate		15
Paraffin wax	0.8	0.6
Calcium stearate	1.75	1.5
Marklube L-126 (ester lubricant)	0.3	0.6
Low molecular weight polyethylene	0.1	0.1

Siding. [Data from **Advastab TM-286 SP**. *Rohm & Haas*.]

Raw material	capstock	substrate
	Concentration, parts	
PVC (K=65-68)	100	100
Paraloid K-120N (process aid)	1-2	1-2
Paraloid KM-399 (impact modifier)	5-8	3-5
Calcium stearate	1-1.5	1-1.75
Advawax 280	1-1.5	
Paraffin wax		1-1.25
Oxidized polyethylene		0.1-0.2
Titanium dioxide	8-12	1-3
Calcium carbonate		2-8
Advastab TM-286 SP (methyltin)	1-1.5	1-1.5

Rigid siding (substrate and capstock). [Data from **Thermolite 172 and 174**. *Arkema*.]

Raw material	substrate	capstock
	Concentration, phr	
PVC (K=65)	100	100
Thermolite 174	0.8-1	
Thermolite 172		0.9-1.2
Calcium stearate	1-1.1	1-1.5
Paraffin wax (melting point=74°C)	1-1.3	1-1.3
Oxidized polyethylene wax	0.1-0.2	
Plastistrength 710		0.5-0.5
Durastrength 510	4.5-5.5	
Durastrength 200 or 200L		5-6
Calcium carbonate (0.8 μm)	7-10	
Titanium dioxide	0.5-1	9-10

PVC siding capstock. [Data from **Zeocros. Specialty zeolites**, *PQ Corporation*, 2011.]

Raw material	Concentration, parts
PVC (K=69)	100
Paraloid KM334	5
Paraloid K120N	1.5
Advastab TM 181	1.25
Paraffin wax 165	1.2
Calcium stearate	1.2
Oxidized polyethylene	0.15
Omya Carb-1 (calcium carbonate)	2
TiO_2	10

4.5.13.2 Formulations found in the open literature

Titanium dioxide – important UV stabilizer of PVC siding. [Data from Yang, T-C, Noguchi, T, Isshiki, M, Wu, J-H, *Polym. Deg. Stab*., in press, 2014.]

Raw material	Concentration, parts
PVC	100
Acrylic polymer	0.7
Paraffin wax	0.5
Organotin mercaptide	0.6
Fatty acid soap	1.5
Titanium oxide	10

Siding capstock. [Data from Girois, S.; Schipper, P. S., *J. Vinyl Additive Technol.*, **7**, 2, 61-66, 2001.]

Raw material	Concentration, parts
PVC	100
External lubricants	1.05
Internal lubricants	0.2
Acrylic lubricant	0.2
Lubricating process aid	0.7
Impact modifier	6.0
Titanium dioxide	10.0
UV stabilizer	0.5
Organotin maleate	3.0

Use of maleate stabilizer opens (according to reference) new possibilities in the production of dark color siding.

Siding capstock and substrate. [Data from Rapacki, S. R., *J. Vinyl Additive Technol.*, **4**, 1, 12-21, 1998.]

Raw material	Capstock	Substrate
	Concentration, parts	
PVC (K=66)	100	100
Tin stabilizer	1.2	0.9
Calcium stearate	1.3	1.3
Paraffin wax	1	1

Siding capstock and substrate. [Data from Rapacki, S. R., *J. Vinyl Additive Technol.*, **4**, 1, 12-21, 1998.]

Raw material	Capstock	Substrate
	Concentration, parts	
Polyethylene wax	0.1	0.15
Titanium dioxide	10	1
Calcium carbonate	3	10
Acrylic impact modifier	5	5
Process aid		1
Lubricating process aid	0.5	0.5

Siding. [Data from Ventresca, D. A.; Berard, M. T., *J. Vinyl Additive Technol.*, **3**, 4, 274-278, 1997.]

Raw material	Content parts
PVC	100
Stabilizer	0.8
Calcium stearate	1.0
Paraffin wax	1.2
High molecular weight PMMA	0.8
Lubricant (fatty acid ester)	0.5
Metal release	0.3
CPE impact modifier	5.0
Oxidized PE	0.2
TiO_2	1
$CaCO_3$	10-20

Impact strength at 23°C – 15.9, at 0°C – 13.0, and at -10°C – 10.4 J/mm

4.5.13.3 Patented inventions

Siding. [Data from Bootier, H, Harris, R, Nesbitt, J, Said, K, **Canadian Patent CA2686305**, May 26, 2010, *Fiber Composites Llc*.]

Raw material	Concentration, parts
PVC (FPC 616)	100
Stabilizer (TM181)	0.8
Lubricant (Paraffin 165)	0.8
Lubricant (PE AC 629A)	0.15
Lubricant (calcium stearate)	0.6

Siding. [Data from Bootier, H, Harris, R, Nesbitt, J, Said, K, **Canadian Patent CA2686305**, May 26, 2010, *Fiber Composites Llc*.]

Raw material	Concentration, parts
Filler (Omya UFT)	0.7
Processing aid (K-400)	6
Titanium dioxide	0.5
Blowing agent (Forte-Cell 247 Azo)	0.8

Siding composition. [Data from Lundquist, E G, Cho, J-Y, **US Patent US8614268**, Dec.24, 2013, *Rohm and Haas*.]

Raw material	Concentration, parts
Solvin K58	75
Vinyl acetate	25
Advalube F1060L (glyceroldioleate)	0.8
Advalube E2100 (pentaerythritol ester lubricant)	0.4
Paraloid BTA-736s (MBS impact modifier)	6
Paraloid K-175 (acrylic processing aid)	0.75
Paraloid K120ND (acrylic processing aid)	0.5
TiO_2	5
Polyacid A	0.25
Alkyl tin stabilizer	1.5

Straight face vinyl siding. [Data from Fairbanks, L. R.; DeWorth, S. W.; Barber, D. C., **US Patent 7,204,062**, Apr. 17, 2007.]

Raw material	Base	Capstock
	Concentration, parts	
PVC	100	100
Tin stabilizer(s)	0.5-2	0.5-2
Process aid(s)	0-2	0-2
Lubricant(s)	1.5-3.5	1.5-3.5
Impact modifier(s)	2-6	2-6
Weathering agent(s)	0.5-12	9-11
Colorant(s)	q.s.	q.s.

4.5.14 TUBING

4.5.14.1 Formulation proposed by the raw material supplier

Beverage tubing. [Data from **Mark 3023**. Technical data sheet. *Chemtura Corp.*]

Raw material	Concentration, parts
PVC	100
DOA or DOP*	35
Drapex 6.8 or 10.4	10-15
Mark 3023 (FDA cleared Ca/Zn stabilizer)	1.5-2
Mark 329	0.5-1
Hystrene 5016 (stearic acid)	0-0.25

*DOP can only be used when the food is of high water content.

4.5.14.2 Patented invention

Tube catheter. [Data from Shon, D M, **World Patent WO2013157846**, Oct. 24, 2013, *Cem Tech. Co. Ltd. Korea.*]

Raw material	Concentration, parts
PVC	100
NBR	20
Plasticizer	80-12
Stabilizer	1-3

Garden hose formulation [Data from Bunting, N.; Lorraine, S., **US20160033060A1**, *Swan Products LLC*, Feb. 4, 2016.]

Raw material	Concentration, parts
Ultrahigh molecular weight PVC (K=79-85)	60
Crosslinked PVC (K=73-75)	40
(2-Propyl heptyl) phthalate	75
Epoxidized soybean oil	10
Calcium stearate	0.15
Zinc stearate	0.35
Irganox 101	0.1
Ethylene bis-stearamide	0.15
Titanium dioxide	0.5

4.5.15 WATER STOP SEAL

4.5.15.1 Formulation proposed by the raw material supplier

Water stop. [Data from **Eastman 168 Plasticizer**. Publication L-187H. *Eastman*, March 2002.]

Raw material	Concentration, parts
PVC resin (medium to high molecular weight)	100
Calcium carbonate	35
Ba/Cd stabilizer (now obsolete)	1
Eastman 168 (plasticizer)	55.8
Eastman TXIB (plasticizer)	6.2

4.5.15.2 Patented inventions

Water-sealing sealant. [Data from Ichizuka, I.; Takahashi, S.; Hara, K.; Waki, H.; Kobe, S.; Sakarada, T.; Okouchi, Y., Ohkubo, K.; Shimizu, H., **US Patent 5,476,718**, Dec. 19, 1995.]

Raw material	Concentration, parts
PVC	100
DOP	100
Stabilizer	2.6
Water-swelling polyurethane	40

The water-swelling polyurethane is a prepolymer obtained from polyoxyalkene (polyether) polyol reacted with isocyanate (ratio 1.1 to 1.7 of isocyanate groups to reactive hydrogens in polyol).

PVC sealing material with low thixotropy. [Data from Nagata, N.; Tsutsui, I.; Ota, A. K.; Hashimoto, H., Shibata, H., **US Patent 5,188,693**, Feb. 23, 1993.]

Raw material	Concentration, parts
PVC (fine particle size: 2-3 μm)	15
PVC (coarse particle size: 20-30 μm)	5
DOP	23
Thixotropic agent (organic bentonite and calcium carbonate)	14
Untreated powdery filler (calcium carbonate)	37
Amine type adhesive promoter	1
Thermal stabilizer	5

4.5.16 WINDOW AND DOOR PROFILE

4.5.16.1 Formulations proposed by the raw material suppliers

Ca/Zn window profile formulation. [Data from **Waxes for PVC Lubrication**. *Clariant*, 2013.]

Raw material	Concentration, parts
PVC copolymer, 7% acrylate copolymer (K=64)	100
Ca/Zn stabilizer	3.4
Phosphite (TNPP)	0.4
PMMA processing aid	2
Hydroxystearic acid	0.2
Licolub WE 40	0.3
Licocene PP 6102/Licowax PE 520	0.2
TiO_2	7
$CaCO_3$	4

Sn window profile (twin screw). [Data from **Waxes for PVC Lubrication**. *Clariant*, 2013.]

Raw material	Concentration, parts
PVC copolymer, 7% acrylate copolymer (K=64)	100
Sn stabilizer containing sulfur	1.5
PMMA processing aid	1
Calcium stearate	1
Glycerol monostearate	0.5
Licocene PE 4201/Licocene PP 6102/Licolub H4	0.6
Licolub WE 4	0.4
Licowax PE 520	0.1
TiO_2	8
$CaCO_3$	3

Window profiles. [Data from *Baerlocher*.]

Raw material	Ca/Zn	Pb
	Concentration, parts	
S-PVC (K=65)	100	100
Impact modifier	7	7
Filler	6	6
Titanium dioxide	3.5	3.5
Baeropan 9935 FP (Ca/Zn stabilizer)	3.5	
Baeropan 51021 FP (lead stabilizer)		5
Process aid	included in stabilizer	

Window profile. [Data from Treffler, B., **Impact of lubricant onto the processing behavior of U-PVC**. *Clariant*. 23.02.2005.]

Raw material	Concentration, parts
S-PVC (K=68)	100
Ca/Zn stabilizer	2.5
Calcium carbonate	5
Titanium dioxide	4
Impact modifier	7
Process aid	1
Fatty acid ester	0.2-0.4
Montanic acid ester wax	0-0.2
Oxidized PE-wax	0.1-0.3
PE/PP wax	0.1-0.25

Window profile. [Data from **Thermolite 170**. *Arkema*.]

Raw material	Concentration, parts
PVC (K=67)	100
Thermolite 170 (butyltin stabilizer)	1-1.5
Calcium stearate	1.2-2
Paraffin wax (melting point=74°C)	1-1.2
Plastistrength 551	0.7-1

Window profile. [Data from **Thermolite 170**. *Arkema*.]

Raw material	Concentration, parts
Plastistrength 710	0.3-0.5
Durastrength 200	5-6
Calcium carbonate (particle size=0.8 μm)	0-5
Titanium dioxide	10

Lead stabilizers are still used for this production in Europe but replacement Ca/Zn stabilizers are available, and their weathering performance is better than that provided by traditional lead stabilizers.

Window profile in white and colors. [Data from *IKA Innovative Kunststoffbereitung GmbH*.]

Raw material	White	Color
	Concentration, parts	
S-PVC (K=65-68)	100	100
Impact modifier	5.5-7.0	5.5-7.0
Coated filler	4-10	4-12
Titanium dioxide	3*	
Pigment		quantum satis
IKA 734 C (Ca/Zn thermal stabilizer)	3.6-4.4	3.6-4.4

*for Western European climate, otherwise 6 phr.

4.5.16.2 Formulations found in the open literature

Window profile. [Data from Weier, J. E., *J. Vinyl Additive Technol.*, **3**, 1, 21-27, 1997.]

Raw material	Contents, parts
PVC (K67)	100.0
TM-181, Sn stabilizer (Morton Thiokol)	1.6
Calcium stearate	1.3
XL-165 lubricant (Hoechst)	1.0
Paraloid K120N (process aid)	0.5
Paraloid K175 (process aid)	1.0
Impact modifier (acrylic)	7.0
Titanium dioxide	10.0

Studies of several impact modifiers show that the critical controlling factors in weld strength are related to the effects of the welding process on blend morphology and modifier orientation.

Profile with green stabilizer. [Data from Trupti, D., *Plastics Additives Compounding*, 44-46, 2004.]

Raw material	Concentration, parts
PVC resin Vinnolit S 3268 (K=68)	100
GreenStab (multicomponent proprietary formulation)	2.6
Titanium dioxide	3.00-5.00
Filler	3.00-5.00
Impact modifier	5.00-7.00
Lubricants	0.8-1.00

GreenStab is a replacement for lead stabilizers used in Europe for window profiles. It is organic stabilizer which does not contain lead and zinc.

Window profile. [Data from Rapacki, S. R., *J. Vinyl Additive Technol.*, **4**, 1, 12-21, 1998.]

Raw material	Concentration, parts
PVC (K=66)	100
Tin stabilizer	1.2
Calcium stearate	1.2
Paraffin wax	1
Titanium dioxide	10
Calcium carbonate	3
Acrylic impact modifier	5
Process aid	1
Lubricating process aid	0.5

PVC window profile for European market. [Data from **Docstoc**]

Raw material	Concentration, parts
PVC (K=65-68)	100
TiO_2	4-7
$CaCO_3$	5-10
Durastrength 300 (acrylic impact modifier)	6-7.5
Dibasic lead phosphate	3

PVC window profile for European market. [Data from **Docstoc**]

Raw material	Concentration, parts
Dibasic lead stearate	0.6
Neutral lead stearate	0.5
Plastistrength 551	0.5-1
Lubricant package	0.5-1

PVC window profile for US market. [Data from **Docstoc**]

Raw material	Concentration, parts
PVC (K=65)	100
TiO_2	10
$CaCO_3$	5
Thermolite 340 (tin stabilizer)	1
Paraffin wax	1
Calcium stearate (lubricant)	1.5
Plastistrength 501 (process aid)	0.5
Durastrength 200 (acrylic impact modifier)	5

4.5.16.3 Patented inventions

Non-toxic window profile. [Data from Jin, D H, Yoon, Y B, Cha, K S, Choi, S H, **World Patent WO2013137688**, Sep. 19, 2013, *Lg Hausys Ltd.*]

Raw material	Concentration, parts
PVC	100
Processing aid	1
Impact modifier	8
TiO_2	4
Calcium carbonate	12
Lubricant	0.5
Non-toxic, metal soap-base stabilizer	2
Zinc coated metal oxide	1
Auxiliary agent	0.2

Door structural member containing wood flour. [Data from Chen, K. Y. W., **US Patent 6,551,537**, Apr. 22, 2003.]

Raw material	Concentration, parts
PVC	100
Wood flour	10-90
Inorganic foaming agent	2.7
Organic foaming agent	0.5
Process aid	12
Property modifier	8
External lubricant	1.5
Internal lubricant	2.5
Inorganic filler	8
Pigment	0.7

Window profile which is cadmium and lead free. [Data from Baumgaertel, H.-G.; van Cleemputte, W.; Waltz, P., **US Patent 5,124,373**, Jun. 23, 1992.]

Raw material	A	B
	Concentration, parts	
S-PVC (K=68)	100	
S-PVC (K=68) containing 8 parts of impact modifier based on butyl acrylate and polymethylmethacrylate		100
Polymethylmethacrylate	1	1
Talc (micronized)	10	
Natural calcium carbonate (ground chalk, surface modified using stearic acid)		10
Titanium dioxide		4
Benzoylstearoylmethane	0.1	0.1
1,4-dihydropyridine	0.2	0.1
Diphenyl decyl phosphite	0.7	
Trilauryl phosphite		0.5
Mixture of di-trimethylolpropane and pentaerythritol		0.5
Calcium stearate	0.8	
Calcium behenate		0.4
Zinc octoate	0.4	0.2
Calcium oxide coated with 2 wt% hydroxystearic acid	0.1	

Window profile which is cadmium and lead free. [Data from Baumgaertel, H.-G.; van Cleemputte, W.; Waltz, P., **US Patent 5,124,373**, Jun. 23, 1992.]

Raw material	A	B
	Concentration, parts	
Magnesium oxide with 2 wt% hydroxystearic acid	0.15	0.25
Mixture of internal and external lubricants containing montan waxes	0.75	0.75
High melting point paraffin wax	0.2	0.1
Partly oxidized high melting point paraffin wax	0.1	0.1

Tin-free window profile. [Data from Heris, C, Uysal, T, Schiller, M, **US Patent US8633266**, Jan. 21, 2014, *Akdeniz Kimya San, Turkey.*]

Raw material	Concentration, parts
PVC (K=67)	100
Titanium dioxide (Kronos 2220)	4
Calcium carbonate (Omya 95T)	7
Acrylic impact modifier (DMA 600)	6
Lubricant (Alkalub 476)	1.8
Antioxidant (Irganox 101)	0.1
Magnesium hydroxide	0.1
Zinc salt (stearate, laurate)	0.3
β-diketone	0.7

Window profile with reduced photoblueing. [Data from Pelzl, B, **World Patent WO2012140054**, Oct. 18, 2012.]

Raw material	Concentration, parts
PVC (K=67)	100
Calcium carbonate	12
High impact acrylate	6
Acrylic processing aid	0.6
Titanium dioxide	3.7
Zn stearate	0.55
Ca stearate	0.5
Tris(hydroxymethyl)isocyanurate	0.2

Window profile with reduced photoblueing. [Data from Pelzl, B, **World Patent WO2012140054**, Oct. 18, 2012.]

Raw material	Concentration, parts
Mg hydrotalcite	0.55
Complex ester wax	0.15
Polyethylene wax	0.05
Ca-acetylacetonate	0.15
12-hydroxy stearic acid	0.1
Glycerin tristearate	0.35
Irgastab 1076	0.1
Organic phosphite	0.07
Hydroquinone	0.015

PVC window profiles containing silver ions [Data from Remizov, A. B., WO2014014382A1, Obshcestvo Organiczennoi Otvetstvennosti "Serviscentr", Jan. 23, 2014.]

Raw material	Concentration, parts
PVC	100
$CaCO_3$	5-16
Lead stabilizer	2-4
Impact modifier	3-6
Titanium dioxide	2-4
Silver nitrate	0.002-0.01

4.5.17 OTHER PRODUCTS

4.5.17.1 Products discussed in open literature

Cellular profiles for Nova block detector. [Data from Richard Talaga, *Argonne National Laboratory*, 2006.]

Raw material	Concentration, parts
PVC (Shintech SE950EG, high reflectivity)	100
Tin stabilizer (Advastab TM-181)	2.5
Titanium dioxide (rutile, DuPont R-102)	19
Calcium stearate	0.8
Paraffin wax (Ferro 165)	1.1
Oxidized polyethylene (Ferro Petrac 215)	0.2
Glycerol monostearate (Rohm & Haas F1005)	0.3

Cellular profiles for Nova block detector. [Data from Richard Talaga, *Argonne National Laboratory*, 2006.]

Raw material	Concentration, parts
Acrylic impact modifier (Arkema Durastrength 200)	4
Processing aid (Paraloid K120N)	1

4.5.17.2 Patented inventions

Extrusion coating of textile with formulation containing dual expanding agents. [Data from Desai, D. R., **US Patent 6,495,206**, Dec. 17, 2002.]

Raw material	Concentration, parts
PVC	136
Filler (Omyacarb)	40.7
Micro-encapsulated blowing agent (Expancel 092)	1
Dispersed blowing agent (Celogen 754A)	4.1
Plasticizer/costabilizer (epoxidized soybean oil)	102
Stabilizer (Nuostab)	3.7
Antioxidant (Irganox)	0.3
Lubricant (Loxiol/Hostalub)	3.3
Process aid (Paraloid K120N)	6.8

Material containing expandable microspheres. [Data from Peretti, G.; Pasetto, R., **US Patent 6,248,799**, Jun. 19, 2001.]

Raw material	Semi-rigid	Flexible
	Concentration, parts	
Suspension PVC	100	100
DOP	20	50
DIDP	15	20
Epoxidized soybean oil	5	5
Stabilizer (Ba/Zn or Ca/Zn)	5.5	5.5
Stearic acid	1	1
Polymeric microspheres containing isopentane	5	5
Azodicarbonamide	0.3	0.3

Railings from a rigid core inserted into tube which shrinks to encapsulate core.

[Data from Coulis, M. L., **US Patent 5,759,660**, Jun. 2, 1998.]

Raw material	Concentration, parts
PVC	100
Linear phthalate plasticizer	23
Titanium dioxide	12
Paraffin wax based process aid	0.4
Polybutyl acrylate	1.3
Heat stabilizer (metal carboxylates)	0.8
Tin based UV stabilizer	0.5
Calcium stearate lubricant	0.5

Medical products.

[Data from Takahashi, H.; Iwata, K., **US Patent 4,869,909**, Sep. 26, 1989.]

Raw material	Concentration, parts
PVC	100
DOP	60
Silica	40
Ca/Zn stabilizer	2

Louver with polished metal look.

[Data from Hawrylko, R. B.; Lakstigala, K.; Asgaralli, A. A., **US Patent 5,496,630**, Mar. 5, 1996.]

Raw material	Concentration, parts
S-PVC	100
Acrylic process aid	1.75
Epoxidized soybean oil	5
Stabilizer (dimethyltin diisooctyl thioglycollate)	1.8
Aluminum flake (Silvex 540, particle size 39 μm)	0.5
Aluminum flake (Sparkle Silvex, particle size 21 μm)	0.6
Stearic acid	0.5
MBS impact modifier	6
Oxidized paraffin wax	0.15

Louver with polished metal look. [Data from Hawrylko, R. B.; Lakstigala, K.; Asgaralli, A. A., **US Patent 5,496,630**, Mar. 5, 1996.]

Raw material	Concentration, parts
Paraffin wax	0.05
Pearl (Afflair 235)	0.1
Pearl (Afflair 135)	0.1
Red	0.04
Blue	0.18
Magenta	0.5
Black	0.25

4.5.18 CONCLUSIVE REMARKS

Extruded products are mostly manufactured without plasticizers (rigid), which includes all major products such as window and door profiles, siding, and pipes, and many other products such as blinds, clear compounds, fencing, interior profiles, planks, and sheets. Semi-rigid formulations are used for medical tools and tubing, and flexible formulations are used to manufacture gaskets, some pipes (e.g., irrigation pipe), some medical tools, and water-stop seals. For this reason, the most typical formulation is that for a rigid product. On the other hand, there are some special needs such as requirements for medical products and products in contact with food which require special raw materials approved by authorities (e.g., FDA). The most common raw materials used in PVC formulations manufactured by extrusion are as follows:

- PVC from medium to ultrahigh molecular weight. PVC is almost exclusively made by suspension polymerization, in most cases extruded from dry blends
- lubricants include a long list of compounds of different origin, such as polyethylene wax, oxidized polyethylene, calcium stearate, stearic acid, paraffin wax, Montan wax, glycerol monostearate, mixtures of fatty acids and alcohols, ester waxes, and white oil
- process aids are mostly acrylic, with two major varieties: process aids and lubricating process aids
- impact modifiers for outdoor use are acrylic and for indoor applications MBS
- calcium carbonate is dominating filler, but limestone, talc, wood flour, microspheres, and glass fibers are also incorporated to serve special needs
- methyltin mercaptide is a dominating thermal stabilizer, but other tin stabilizers are also used as well as zinc stabilizer, Ca/Zn stabilizers, and more seldom (but still) lead stabilizers, with preference given to tribasic lead sulfate
- typical costabilizers include phosphites and epoxidized oils

- modern stabilizing methods do not include metal stabilizers at all but combinations of perchlorates, amine, 1,3-dimethyl-4-aminouracil supported by epoxidized oils and phosphites
- the role of UV stabilizer is played by carbon black and titanium dioxide with the different mechanisms of their action

Other, less commonly used additives, include:

- plasticizers which may be chosen from a broad range of polymeric and monomeric compounds with particular attention given to various toxicity indicators and sources including natural products which can be easily obtained from recoverable sources
- microbiocides including salts of pyroborate and metaborate, and organic compounds
- smoke suppressants, such as zinc oxide, zinc pyrophosphate, magnesium hydroxide, and molybdenum trioxide
- melt strength additives and promoters
- the blowing agent is mostly azodicarbonamide
- some thixotropic agents, such as, for example, bentonite, are also used in flexible formulations
- some blends with chlorinated polyethylene, polymethylmethacrylate, and polyurethane have also found applications

The most important properties of extruded products and formulations used for extrusion include:

- impact strength (all major products contain impact modifier, which is understandable considering that rigid formulations already have outstanding mechanical performance which can be further improved by the addition of impact modifier)
- lubrication (selection of the type and concentration of lubricants is the major task of formulator which determines product quality and production efficiency; many examples in the above tables offer a good background for such selection)
- UV stabilization (the original idea of stabilization by addition of high doses of titanium dioxide was conceived for extruded products used outdoors, and it is essential for their use and performance)
- thermal stabilization (many options are available, and selection is largely driven by health and safety requirements rather than performance since many available stabilizing systems are excellent performers)

Many production problems are solved by adjustments in process parameters, elimination of mechanical breakdown, and cleaning parts of equipment. But there are also many instances when production quality and rate can be restored by adjustments in formulation. Here are examples:

- flow rate instability also called surging (it can be remediated by equipment controls and screw selection but it is also a formulation problem which requires one to look at polymer quality, polymer grade used, too high filler load, wrong proportions between external and internal lubricants)

- variation of product quality (changes in molecular weight of polymer or composition of formulation which may be caused by variability of resin or variability in regrind quality or amount)
- streaks (contamination, dirty die, variability in regrind, change of color, or insufficient mixing)
- dull streaks (contamination of dry blend; plate-out, which is an accumulation of additives on die lips)
- milky areas of poor clarity (contamination with another polymer)
- sharkskin (too high resin viscosity)
- variation in product strength (thermal degradation due to too high temperature or too long residence time, insufficient stabilization, or insufficient lubrication)
- color changes (cleaning required, thermal degradation, reduction of regrind required)
- black specs (foreign material, degraded polymer)
- holes (air entrapment, resin contamination generating gases, degradation of formulation component producing gases, too high moisture content in the formulation, an admixture of previously extruded product)
- pitting or foaming (too high resin moisture)
- silvery streaks (high moisture in resin)
- surface scratches in the machine direction (degraded resin on die lips, too high moisture in resin [see silver streaks])
- fisheyes (some polymer particles do not melt, dirt, contamination with another polymer)
- knit lines (too high molecular weight of the polymer, contamination)
- weak film (melt strength insufficient,
- warpage (molecular orientation, filler or fiber orientation, asymmetric crystallinity)
- surface contamination (product is loaded with static electricity and attracts dirt)
- inferior transparency (contamination, regrind problem, degradation).

Further reading:

Giles, H. F.; Wagner, J. R.; Mount, E. M, **Extrusion. The Definitive Processing Guide and Handbook**, *William Andrew Publishing*, Norwich, 2005.

4.6 FIBER AND THREAD COATING

PVC plastisols and latexes are involved in the production of many useful products, including protection of scrim glass fabric used for reinforcement of cementitious boards and other products, production of breathable fabrics woven from coated fibers, fiber optics, and production of various articles (e.g., fishing lines or tennis racket strings) from coated fibers and threads. Some examples are given below.

4.6.1 PATENTED INVENTIONS

Fabric reinforcement. [Data from Porter, J. F.; Roberts, G., **US Patent 7,354,876**, Apr. 8, 2008.]

This and many other patents make use of glass fiber fabric for reinforcement of cementitious boards without disclosing the formulation. Concrete is a basic material which causes fast deterioration of E-glass fiber; therefore the glass fiber surface must be protected by a surface finish (coating). Such a coating has acidic properties which enhance adhesion to concrete and prevent fiber deterioration. This method has been used for close to 40 years, but little is known about the process in the patent literature. The following patent sheds some light on preparation.

Glass fiber substrates coated with PVC. [Data from Peltier, G.; Longuet, M.; Midgley, C. A., **US Patent 4,500,591**, Feb. 19, 1985.]

Raw material	Concentration, parts
PVC	100
Plasticizer	70
Filler (calcium carbonate)	50-150

The above formulation is very general because the patent is for foam rubber backing for a composite material (woven or non-woven glass fabric coated with PVC). In this invention, the fabric is coated mainly to hold woven fibers in position to provide a stable mesh for further processing and use. It should be noted that similar processes may also be used to manufacture mesh such as that used in window screens.

Glass strand coated with PVC plastisol. [Data from Blanchard, B, Chuda, K, **US Patent US20140017471**, Jan. 16, 2014, *Saint-Gobain Adfors*.]

Raw material	Concentration, wt%
PVC	62.5
Butyl benzyl phthalate	31.5
Stabilizer	1
3-Glycidoxypropyltrimethoxy silane	5

Fiber optic cable. [Data from Guenter, C, Register, J, Rhyne, T, **World Patent WO2009154712**, Dec. 23, 2009, *Corning Cable Systems Llc*.]

A fiber optic cable is an indoor/outdoor drop cable having a UV-resistant, fungus-resistant, riser rated PVC outer jacket. The outer jacket can be made from PVC available from Georgia Gulf Corporation under the product designation Georgia Gulf 16882 Coax and Telecom Flexible PVC, and may have a jacket elongation of at least 270%. The jacket elongation may fall in the range of 300-350% according to one application. The outer jacket includes additives to increase its UV light resistance and fungus resistance. The maximum brittleness temperature is -35°C. The relatively low brittle point temperature may help the cable to conform with industry standard cold impact tests as well as affording greater flexibility for ease of installation in low-temperature environments.

Fly fishing line. [Data from Kauss, D. A.; Richards, B. W., **US Patent 6,321,483**, Nov. 27, 2001.]

Raw material	Concentration, parts
PVC (Geon 121)	100
DOA	14
Epoxidized 2-ethylhexyl tallate (Monoplex S-73)	16
Diundecyl phthalate	25
Silicone oil (DC-200)	5
Ba/Zn stabilizer (SYN-940)	2
UV absorber (Uvinol 3039)	0.8
Glass microspheres (G18/500)	0.004
Fluorochemical for improved hydrophobicity (FC-3537)	0.001
Polytetrafluoroethylene (MP-100)	0.0016

The last two additives prolong the life of fishing line by lowering the coefficient of friction.

Buoyant fishing line. [Data from Martuch, L. L., **US Patent 3,936,335**, Feb. 3, 1976.]

Raw material	Concentration, parts
PVC (Geon 121)	100
DOA	53
Epoxidized tall oil (Flexol EP8)	10
Lead soap (now obsolete)	3

A similar concept of fiber bundle coating can be used for the production of raw material for weaving textiles and mesh useful in many applications such as garden furniture, office chairs, sports equipment, etc. The coating protects fiber, fiber gives a mechanical performance, and free space between coated fibers allows for free air exchange, giving high comfort in products' use.

4.7 FILM PRODUCTION

Film production is discussed in a separate section because it involves several different methods of production, although patents mostly involve calendered films. The application examples given in this section differ from examples given in the calendering section. Emphasis is given to application and film structure as it relates to application needs.

4.7.1 FILM

4.7.1.1 Formulation proposed by the raw material supplier

Crystal-clear film. [Data from **Mark 275**. Technical data sheet. *Chemtura Corp*.]

Raw material	Concentration, parts
PVC (low to medium molecular weight)	100
Impact modifier	0-10
Acrylic process aid	0-5
Mark 275 (sulfur-free organotin)	2-3
Calcium stearate	0.5-1

Clear rigid PVC starting point formulation from BASF

Raw material	Concentration, parts
SPVC	100
Impact modifier (MBS)	0-5
Ca/Zn stabilizer	2-3
Epoxidized soybean oil	1-1.5
Wax	0.2-0.4
Lubricants	0.2-0.5
Processing aids	0.5-1
UVA	0.25-1

4.7.1.2 Patented inventions

Interlayer PVC film for safety glass. [Data from Purvis, M. B.; Parker, A. A.; Holmes, P. A.; MacLachlan, J. B.; Scott, J. R.; Negishi, Y., **US Patent 6,180,246**, Jan. 30, 2001.]

Raw material	Concentration, parts
PVC (SE1300 from Shintech)	95
Copolymer of 90% VC and 10%VAc (MPR-TSN from Nissin Chemicals)	5
DOA	50
Epoxidized soybean oil (Drapex 6.8)	5
Ba/Zn stabilizer (Thermchek 130)	3
Antioxidant (Irganox 1010)	1
Perchlorate stabilizer (CPL-46)	0.15
UV stabilizer (Tinuvin 328)	0.2
Adhesion (Pummel)	9
Impact (MBH) at -18°C	13’
Impact (MBH) at 23°C	19’
Impact (MBH) at 60°C	12’
Haze, %	0.8
Initial yellowness index, YI	0.8
Heat stability (YI after 500 h at 100°C oven)	11.5
Optical quality	good

4% solution of silane (N-[β-(N’-para-vinylbenzyl)-aminoethyl]-γ-aminopropyltrimethoxy silane hydrochloride, known as Z6032 from Dow Corning) was used as an adhesion promoter.

Self-adhering safety glass interlayer. [Data from Parker, A. A.; Bartus, S. P.; Wolke, S. M., **US Patent 5,593,786**, Jan. 14, 1997.]

Raw material	Concentration, parts
PVC (SE1300 from Shintech)	70
VC/VAc (94/6 copolymer (Geon E8)	20
Polycaprolactone (CAPA 656)	10
Dihexyl adipate	40
Epoxidized soybean oil (Drapex 6.8)	5
Ba/Zn stabilizer (Thermchek 130)	3
Antioxidant (Irganox 1010)	0.5
Perchlorate stabilizer (CPL-46)	0.1

Self-adhering safety glass interlayer. [Data from Parker, A. A.; Bartus, S. P.; Wolke, S. M., **US Patent 5,593,786**, Jan. 14, 1997.]

Raw material	Concentration, parts
UV absorber (Tinuvin 238)	0.25
Adhesion (Pummel)	9
Haze initial, %	0.5-0.8
Initial yellowness index	0.5
Refractive index (adhesive/support layer)	1.521/1.546
Heat stability (YI after 500 h at 100°C oven)	5.6
Optical quality	no visible distortion

Image printed inside safety glass. [Data from Matarazzo, P, **World Patent WO2013050819**, Apr. 11, 2013.]

The process of production comprises the following steps: preparing two sheets of float (or tempered) glass of a predetermined size; printing image onto a support material made out of a soft PVC film; assembling a sandwiched structure with each component according to the following arrangement: a first glass sheet; a first layer of EVA adhesive; printed PVC film; a second layer of EVA adhesive; and a second glass plate. The sandwiched structure is placed in an oven having a temperature of 130°C±20°C, and kept until the sandwiched structure is completely stratified.

Flexible film for medical applications. [Data from Carmen, R. A.; Bauman, R. H., **US Patent 6,060,138**, May 9, 2000.]

Raw material	Concentration, parts
Ultrahigh molecular weight PVC (K=78-93)	100
Plasticizer (tri-(2-ethylhexyl) trimellitate)	120
Epoxidized soybean oil	5
Ca/Zn stabilizer	0.32
Mineral oil	0.2
O_2 transmission rate, µmoles/h at 22°C	27.8

Bags produced with the same plasticizer but without the benefit of this invention have an oxygen transmission rate of 12.9 at the same conditions as listed in the table.

Antibacterial film for food packaging. [Data from Watanabe, T.; Aoki, S.; Ohta, S.; Shirono, K.; Tanaka, A., **US Patent 5,929,133**, Jul. 27, 1999.]

Raw material	Concentration, parts
PVC	100
Diisononyl adipate	20
Epoxidized linseed oil	10
Stabilizer	1
Hydrotalcite	0.1
Polyglycerin fatty acid ester	1
Silver zeolite antibacterial agent (Atomy Ball)	0.4

Printable self-clinging film. [Data from Nguyen, B. T.; Matsumoto, T.; Katagiri, T., **US Patent 5,698,621**, Dec. 16, 1977.]

Raw material	Concentration, parts
PVC (SE-950 from Shintech)	100
Butyl benzyl phthalate	55
Epoxidized soybean oil	2
Ba/Zn stabilizer (UBZ-791 from Baerlocher)	2
Pigment (Violet 13)	0.07

Optical modification of PVC film with biobased polymer. [Data from Kann, Y, Weinlein, R, **US Patent US20140051787**, Feb. 20, 2014, *Metabolix, Inc*.]

Raw material	Concentration, parts
PVC (K=70)	100
Poly-3-hydroxybutyrate-co-4-hydroxybutyrate copolymer	28
BaZn solid stabilizer	2.5
Epoxidized soybean oil	4.5
Phosphite (HiPure 4)	0.5
Trigonox 117	0.1
Pentaerythritol	0.1

Biodegradable and compostable white opaque PVC film [Data from Klaus, W. M.; Marco, P.; Nair, A. S.; Naik, P., **EP2766275A4**, *Bilcare Ltd,* Aug. 5, 2015.]

Raw material	Concentration, parts
Suspension PVC	252.75
VC/VAc copolymer	49.9
Methylmethacrylate-butadiene-styrene terpolymer	16.94
PVC emulsion polymer	39.5
Polyol-based lubricant	1.5
Amide of ethylenediamine	0.5
Acrylic processing aid	2.06
Bio-pro-degradant (Eco-pure)	4
Titanium dioxide	1.4
Stabilizer	3.75
Partial ester of fatty acids with glycerol	3.04

Phosphorescent film. [Data from Nguyen, B. T.; Katagiri, T., **US Patent 5,374,377**, Dec. 20, 1994.]

Raw material	Concentration, parts
PVC (SE-950 from Shintech)	100
Epoxidized soybean oil	6
Diisononyl phthalate	60
Zn stearate	1
Tertiary phosphite (Mark 1500)	3
Phosphorescent pigment (zinc sulfide phosphor)	200

The formulation gives very bright initial afterglow which has a duration of over 2 hours.

Antistatic/antifogging film. [Data from Fahey, T. E.; Falter, J. A., **US Patent 5,149,724**, Sep. 22, 1992.]

Raw material	Concentration, parts
M-PVC	100
Ca/Zn stabilizer (Synpro 1566)	1
Phosphite (Synpro 241)	1
Epoxidized soybean oil	10

Antistatic/antifogging film. [Data from Fahey, T. E.; Falter, J. A., **US Patent 5,149,724**, Sep. 22, 1992.]

Raw material	Concentration, parts
Plasticizer (PX-238)	35
Triglycerol monooleate	1.25
Polyoxyethylene sorbitan monooleate	1.25

Sterilizing medical grade film. [Data from Arena, A. A., **US Patent 5,011,660**.]

Raw material	Concentration, parts
PVC	100
Di-(2-ethylhexyl) phthalate	33
Organozinc stabilizer (Mark QTS)	0.75
Epoxidized soybean oil	15
Barium sulfate	4.47
Stearic acid (Industrene 7018 FG)	0.25

The film was successfully sterilized with 1 to 5 megarads of γ-radiation without a color change.

PVC film. [Data from Wildenau, A., **US Patent 4,579,907**, Apr. 1, 1986.]

Raw material	Concentration, wt%
PVC	77.6
Ethylene vinyl acetate carbon monoxide terpolymer	19.4
Process aid	3
Tensile strength, N	350
Elongation at break, %	235

The film is internally plasticized and therefore does not fog. This formulation was used to produce double layer film for automotive applications.

Delustered film. [Data from Zenter, E.; Bingemann, W., **US Patent 4,454,294**, Jun. 12, 1984.]

Raw material	Concentration, parts
PVC (K=60)	100
Titanium dioxide	5
Heat stabilizer	1.5
Lubricant	0.7

The formulation is simple. The effect of delustering was achieved by a proper combination of surface finish of calender rolls and conditions of their operation which are described in detail in the invention along with several other examples.

Heat-shrinkable film. [Data from Yoshiga, N.; Nakamura, H.; Ohmura, M., **US Patent 4,264,010**, Apr. 28, 1981.]

Raw material	Concentration, parts
PVC	100
Dibutyltin maleate	4
Lubricant	0.7
Plasticizer	15
VC/VAc (85/15) copolymer	14

Film of high moisture barrier properties. [Data from Bennington, R. L.; Messengale, J. T., **US Patent 4,088,725**, May 9, 1978.]

Raw material	Concentration, parts
PVC	100
Organotin heat stabilizer	1.5
DOP	30
Epoxidized soybean oil	5
Extrusion lubricant	0.15
Paraffin wax (Sunwax 4412)	1.5

Proper annealing conditions influencing paraffin wax distribution determine moisture vapor transmission rate.

4.7.2 FOOD WRAP

4.7.2.1 Formulations proposed by the raw material suppliers

Non-toxic film. [Data from **Mark 3023 and Mark QTS**. Technical data sheet. *Crompton*.]

Raw material	General purpose	Non-fogging
	Concentration, parts	
PVC	100	100
DOA or DOP*	20-40	20-40
Drapex 6.8 or 10.4	10-15	10-15
Mark 3023	2-3	
Mark 329	0.-1	
Mark QTS		0.25-1
Mark 1178		0.5-1
Marklear AFL-3		3-5
Hystrene 5016 (stearic acid)	0-0.25	0-0.25

*DOP can only be used when the food to be packaged is of high water content.

Food wrap. [Data from **Drapex 6.8. PVC secondary heat stabilizer/secondary plasticizer**. *Chemtura*.]

Raw material	Concentration, parts
Homopolymer resin	100
DOA	20-40
Drapex 6.8 (epoxidized soybean oil)	15
Mark 329 (thermal stabilizer)	0.5-1
Mark 152 (thermal stabilizer)	1.5-2
Markclear antifogging agent AFS-18	3-5

4.7.2.2 Patented invention

Food wrap. [Data from Gott, S. L.; Olsen, D. J., **US Patent**, **6,675,560**, Jan. 13, 2004.]

Raw material	Concentration, parts
PVC (Oxy 240F)	100
DOA	10.75
DOP	32.25
Epoxidized soybean oil	5
Ca/Zn stabilizer (Mark QTS)	1
Ca/Zn stabilizer (Interstab CZL-720)	0.5

Food wrap. [Data from Gott, S. L.; Olsen, D. J., **US Patent**, **6,675,560**, Jan. 13, 2004.]

Raw material	Concentration, parts
100% modulus, MPa	12.94
Tensile strength, MPa	20.63
Elongation at break, %	304.2
Tear resistance, kN/m	89.6
Brittleness temperature, °C	-38
Torsional stiffness at 35,000 psi, °C	-29.1
Cottonseed oil extraction, wt% loss	4.93

4.7.2.3 Formulations found in the open literature

Food wrap based on natural products. [Data from Munhoz, D. R.; Moreira, F. K. V.; Bresoli, J. D.; Bernardo, M. P.; De Sousa, C. P.; Mattoso, H. C., *ACS Sustainable Chem. Eng.*, **6**, 9883-92, 2018.]

Edible films may replace non-biodegradable materials in conventional packaging systems. PVC cling film which is in widespread use today is one of the targets for this replacement. The non-PVC wrap film was produced from 50/50 mixture of pectin and rind obtained from yellow passion fruit (*Passiflora edulis Sims f. f lavicarpa* degener) forming 6 wt% water solution by continuous casting at a wet thickness of 1.7 mm and drying at 120°C. The cling film is biodegradable which is an environmental improvement over PVC, but it also means that food preservative may be needed. The wrap film is partially made from waste biomass, and it has performance characteristics similar to PVC cling film (which is much thinner (about 10 times) than the bio-based film).

4.7.3 CONCLUSIVE REMARKS

A general formulation of PVC film includes the following primary ingredients:

- PVC (usually low to medium molecular grade but ultrahigh molecular weight PVC was also used)
- thermal stabilizer (tin (usually sulfur-free), Ca/Zn, and Ba/Zn)
- costabilizer (epoxidized oil, phosphite, hydrotalcite)
- lubricant (because different methods of production are used, different ranges of concentrations and types of lubricants are used, such as stearic acid, calcium stearate, mineral oil, polyglycerin fatty acid ester, triglycerol monooleate, polyoxyethylene sorbitan monooleate, paraffin wax, and many other)
- acrylic process aid

Other optional components of formulation depend on the application of film, and they include the following raw materials:

- plasticizers (these include phthalates, adipates, and trimellitates in concentrations from 0 to 120 phr)

- impact modifier (usually acrylic)
- biocides in food and medical applications (e.g., Ag-zeolite)
- special pigments (e.g., phosphorescent pigment in phosphorescent film)
- barium sulfate in radiation sterilized film
- adhesion promoter (silane) in safety glass applications
- antistatic, slip, and antifogging compounds

The following are the most critical attributes of films:

- mechanical performance (it depends on formulation but also thickness)
- clarity (many factors influence film clarity, including compatibility of formulation components, refractive indices of components, the presence of dirt, reaction to water, conditions of processing and presence of moisture in materials being processed, and many others)
- required surface properties vary with applications (e.g., adhesion in laminating films, slip or clinging in a packaging application, antistatic in medical and electronic applications, heat sealability, etc.)

Troubleshooting directions related to formulation are discussed in sections devoted to calendering and extrusion.

4.8 FOAMING AND FOAM EXTRUSION

Several processing methods use foaming as part of the manufacturing process. These methods and their products are included here, except for coated fabrics, which also contain a foamed layer. Coated fabrics are discussed in the section on web coating.

4.8.1 FORMULATIONS PROPOSED BY THE RAW MATERIAL SUPPLIERS

Foamed profile. [Data from **Foamed profiles**. *Baerlocher*.]

Raw material	Concentration, parts
S-PVC (K=57-60)	100
Coated filler	5
Titanium dioxide	4
Process aid (high molecular weight)	5-6
Lubricant	0.1-0.5
Baeropan R 9964	4.5-5
Blowing aid	quantum satis

Starting point formulations proposed by PolyOne. [Data from **Cellular PVC Products**. Technical Assistance Brief # 019. August 2001. *PolyOne*.]

Raw material/Property	Low*	Medium*	High*
	Concentration, parts		
Geon 121A	80		
Geon 180X7		80	
Geon 180X5			100
Geon 213	20	20	
Palatinol 711P (C7-11 phthalate)	65	65	70
Paraplex G 62 (epoxidized soybean oil)	5	5	
Actafoam R 3 (kicker)	1	2	3
Kempore SD 125 (azodicarbonamide-based)	2	6	16
Gelation temperature, °C	107+	107+	97
5 min at 177°C; expansion ratio density, pounds/cubic feet	3.0 33.6	6.1 14.3	10 8.25
3 min at 191°C; expansion ratio density, pounds/cubic feet	4 25.5	6.7 12.6	11 6.85

Starting point formulations proposed by PolyOne. [Data from **Cellular PVC Products**. Technical Assistance Brief # 019. August 2001. *PolyOne*.]

Raw material/Property	Low*	Medium*	High*
	Concentration, parts		
2 min at 204°C; expansion ratio density, pounds/cubic feet	3.8 26.1	6.1 13.5	12 6.35
3 min at 204°C; expansion ratio density, pounds/cubic feet	3.6 27.4	6.8 12.6	12 6.2

*density

Foam formulations for different processes. [Data from **Celogen Foaming Agents. Flexible Vinyl Foam Applications**. *Chemtura Corp*. 09/10/02.]

Raw material	LFT[a]	CPF[b]	RM/SM[c]	PM[d]
	Concentration, parts			
PVC (K=75)	100			
PVC (K=72)		100		
PVC (K=65) dispersion			70	100
PVC (K=60) blending			30	
DOP	80-95	75	70	95
Benzyl butyl phthalate		20		
Epoxidized soybean oil	5	5	1.6	10
Stabilizer[1]	3			
Stabilizer[2]		3		
Stabilizer[3]				3.5
Zinc oxide			0.5-1	
Phosphite chelator		1		
Celogen OT				30
Celogen AZ		3-5		
Titanium dioxide		4		10
Stearic acid		0.3		

a – low fusion temperature, b – calender processed foam, c – rotational molding/slush molding, d – pressure molding; 1 – stabilizer selection depends on required properties because Celogen OT is not significantly affected by stabilizers, 2 – in original formulation Ba/Cd stabilizer was used (now obsolete), 3 – pressure molding requires long time 20-30 min at temperatures 163-177°C therefore good stabilization is important, also high levels of foaming agent are required.

Crompton gives several important suggestions regarding corrective measures of foam defects, as follows:

- Surface roughness, blisters, and collapsed foam may be caused by undispersed foaming agent particles, poorly matched plastisol fusion rate and decomposition rate of foaming agent, or high ambient humidity. Some of the solutions are to predisperse the foaming agent in plasticizer before its addition to plastisol, use plasticizers with higher solvating power (e.g., benzyl butyl phthalate) to decrease fusion temperature, use less potent kicker or less kicker, or use larger particle size of foaming agent to reduce decomposition rate, or add drying agent/moisture scavenger to the plastisol
- Large irregular cells may be caused by plastisol being for too long at a fluid state, which can be corrected by reducing residence time or the addition of polymeric plasticizer to increase melt viscosity
- The too high density of foam may be caused by too low concentration of foaming agent, too short residence time in an oven or too slow decomposition rate of foaming agent for the fusion rate of plastisol. The problem can be remediated by an increased level of the foaming agent, increased temperature or residence time, or addition of more kicker or faster kicker

Sheet (free-foamed and Celuka). [Data from **IKA Innovative Kunststoffbereitung GmbH**.]

Raw material	free foamed	Celuka
	Concentration, parts	
PVC suspension or mass (K=58)	100	
PVC suspension (K=58-65)		100
Impact modifier	6-10	4-7
Process aid	2-6	6-10
Coated filler	4-6	0-4
Blowing agent		0.5-2
Pigment	quantum satis	quantum satis
IKA 750C (Ca/Zn stabilizer)	5-8	
IKA 760 C		6-8

PVC Foam sheet & profile formulation [Data from Paraloid K-series, DowDuPont.]

Raw material	Concentration, parts
PVC (K=57-60)	100
Advastab TM-950F	1.7-2
Paraloid K400P	7-10
Paraloid K175P	1-2
Calcium stearate	0.6-1.2
Paraffin wax	0.5-1
OPE wax	0.1-0.2
Sodium bicarbonate	1-1.5
Azodicarbonamide	0.2-0.5
Titanium dioxide	1-5
Calcium carbonate	3-5

4.8.2 FORMULATIONS FOUND IN THE OPEN LITERATURE

Rigid PVC foam. [Data from Decker, R. W., *J. Vinyl Additive Technol.*, **2**, 2, 121-124, 1996.]

Raw material	Concentration, parts
PVC (K=60)	100
Dibutyltin oxide complex	1.5
Azodicarbonamide	0.6
Calcium stearate	0.5
Oxidized polyethylene	0.1
Acrylic impact modifier	6
Treated filler	5
Titanium dioxide	1
Costabilizing ester lubricant (Loxiol VGE 2063)	1
Foam density, g cm^{-3}	0.35

Lubricant type was found to be very important for ease of processing, but it also determined the effectiveness of the blowing agent and the final density of the foamed material. Synergistic effect of lubricant on the blowing agent produces lower foam density.

Rigid PVC foam. [Data from Azimipour, B.; Marchand, F., *J. Vinyl Additive Technol.*, **12**, 2, 55-57, 2006.]

Raw material	Concentration, parts
PVC (K=58)	100
Tin stabilizer	0.6
Azodicarbonamide	0.65
Calcium stearate	1
Paraffin wax	0.5
Process aid	4
Lubricating process aid	0.5
TiO_2	1
$CaCO_3$	5

Sheet (Celuka process and free-foam). [Data from Rapacki, S. R., *J. Vinyl Additive Technol.*, **4**, 1, 12-21, 1998.]

Raw material	Celuka	Free foam
	Concentration, parts	
PVC (K=58)	100	
PVC (K=61)		100
Tin stabilizer	2	1.5
Azodicarbonamide	0.2	0.65
$NaHCO_3$	2	
Calcium stearate	0.6	0.5
Paraffin wax	0.3	1.2
Polyethylene wax		0.15
Epoxidized soybean oil	1	
Titanium dioxide	9	8
Calcium carbonate		5
Lubricating process aid	1	1
High molecular weight process aid	7	6

Skin/core foam. [Data from Rapacki, S. R., *J. Vinyl Additive Technol.*, **4**, 1, 12-21, 1998.]

Raw material	Core	Skin
	Concentration, parts	
PVC (K=67)	100	100
Tin stabilizer	0.8	0.4
Azodicarbonamide	0.3	
Calcium stearate	0.7	0.8
Paraffin wax	1.4	1.2
Polyethylene wax		0.1
Titanium dioxide	0.75	1.5
Calcium carbonate	5	5
Acrylic impact modifier		3
Process aid		0.8
Lubricating process aid	1	
High molecular weight process aid	3	

Rigid foam sheet. [Data from Noreen, L T, **Blowing agents and foaming processes 2006,** Munich, Germany, paper 10, p. 3.]

Raw material	Concentration, parts
PVC (K=57-60)	100
Tin stabilizer	1-2
Epoxy stabilizer	1-2
Lubricants (internal and external)	1.5-2.5
Acrylic process aid	6-10
Blowing agent (ADC)	0.4-0.8
Filler (calcium carbonate)	4-8

The light-weight, high strength, cost-effective composite for industrial applications in aerospace, defense, marine, transportation, and construction. [Jiang, Z.; Du, Z.; Xue, J.; Liu, W.; Li, M.; Tang, T., *J. Appl. Polym. Sci*., **135**, 46141, 2018.]

Raw material	Concentration, parts
PVC (PSH-30)	600
Toluene-diisocyanate	100
Polymeric methylene diphenyldiisocyanates	260
Azodiisobutyronitrile	55
Azodicarbonamide	11
Trimellitic anhydride	80

Rigid crosslinked poly(vinyl chloride) foams formed by semi-interpenetrating network structure *via* the reaction of phthalic anhydride and diisocyanate are widely used in wind turbines, marine, aircraft, and vehicle applications due to their high strength-to-weight ratios, excellent insulation properties, low water absorption, and good chemical resistance. If the foam is made without the addition of phthalic anhydride, a large amount of foaming agent is needed and uneven form structure results. The modified route includes the addition of anhydride which leads to the formation of imide structure and reaction with water gives two molecules of carbon dioxide from one molecule of water which helps to save some blowing agent. At the same time, defects are formed in the crosslinked network structure which result in decreased mechanical performance. The crosslinking reaction can be influenced by the type of anhydride. The use of trimellitic anhydride in place of phthalic anhydride helps to avoid the formation of imide structure and defects in the crosslinking structure. The anhydride group linked to the saturated structure does not cause the formation of imide structure after reacting with diisocyanate and water.

Peroxide crosslinked PVC foam. [Data from Yáñez-Flores, I. G.; Ibarra-Gómez, R.; Rodriguez-Fernández, O. S.; Gilbert, M., *Eur. Polym. J*., **36**, 10, 2235-41, 2000.]

Raw material	Concentration, parts
PVC V-124	100
DOP	80
Azodicarbonamide	2
Ca/Zn stabilizer	4
Ba/Cd kicker	4

Peroxide crosslinked PVC foam. [Data from Yáñez-Flores, I. G.; Ibarra-Gómez, R.; Rodriguez-Fernández, O. S.; Gilbert, M., *Eur. Polym. J.*, **36**, 10, 2235-41, 2000.]

Raw material	Concentration, parts
Peroxide	2
Trimethylolpropane-trimethacrylate	10

The peroxide/trimethylolpropane-trimethacrylate system allows the formation of a highly dense network, due to the trifunctional nature of the crosslinking co-agent. The resultant foam does not contain residual unsaturation after the optimum curing time. The thermal stability of the foamed samples was always better than that of the commercial foam examined.

4.8.3 PATENTED INVENTIONS

Foamed composites containing wood flour. [Data from Chen, K. Y. W., **US Patent 6,380,272**, Apr. 30, 2002.]

Raw material	Concentration, parts
PVC	100
Wood flour	10-90
Thermal stabilizer (tin or Ba/Zn)	2.5
Foaming assistant (MgO or ZnO)	1.2
Foaming agent (azodicarbonamide)	0.5
Inorganic foaming agent (sodium bicarbonate)	1.5
Process aid (acrylic or ethylene vinyl acetate)	1.2
Polyethylene wax	8
External lubricant (fatty acid or its ester)	1.5
Internal lubricant	2.5
Filler (calcium carbonate)	8
Pigment	0.7

Acrylic process aid for PVC foam extrusion

Raw material	Concentration, parts
PVC (K=57)	100
Tin stabilizer (Thermolite 161)	2.5
Calcium stearate	0.7
Paraffin wax	1
Oxidized polyethylene wax	0.2

Acrylic process aid for PVC foam extrusion

Raw material	Concentration, parts
High molecular weight process aid (this invention)	7.5
Low molecular weight process aid (Plastistrength 770)	2
Filler (treated calcium carbonate)	5
Foaming agent (azodicarbonamide)	0.5

PVC foam with improved moldability [Data from Kim, Y. H.; Kim, G-S; Lee, K. J., **US9670349B2**, *LG Chem Ltd*, Jun. 6, 2017.]

Raw material	Concentration, parts
PVC (LG080)	100
PVC foam processing aid	4
Thermal stabilizer (OTL-9)	4
Calcium carbonate	7
Lubricant	2
Titanium dioxide	2
Azodicarbonamide	0.7

Thermoplastic foam. [Data from Shin, B. S.; Lee, J. Y.; Kim, D. K.; Cho, S. O., **US Patent 5,776,993**, Jul. 7, 1998.]

Raw material	Concentration, parts
E-PVC	20
S-PVC	80
DOP	45
Epoxidized soybean oil	45
Acrylic impact modifier	20
Acrylic process aid	10
Butyl stearate	5
Ca/Zn stabilizer	2
Foaming agent (combination of azodicarbonamide, p,p’-oxy(benzenesulfonyl hydroxide), and p-toluenesulfonyl hydrazine)	6
Calcium carbonate	20

Plastic laminate. [Data from Kitazawa, K.; Nakamura, E., **US Patent 5,350,550**, Sep. 27, 1994.]

Raw material	Concentration, parts
PVC	100
DOP	60
Calcium carbonate	80
Titanium dioxide	15
Azodicarbonamide	5
Na/Zn thermal stabilizer	3
Mineral spirits	10

PVC foamed board [Data from **CN105647054A**, Jun. 8, 2016.]

Raw material	Concentration, parts
PVC	75
Stabilizers	3
Modifiers	8
Calcium carbonate	40
Brighteners	0.04
Titanium dioxide	3
Ultramarine	0.015
Blowing agent	0.4
Internal lubricants	0.7
External lubricant	0.4
Plasticizer	0.9

Rigid foam. [Data from Ou, J.-W., **US Patent 5,238,966**, Aug. 24, 1993.]

Raw material	Concentration, parts
VC/VAc copolymer	100
EVA copolymer	5-50
Acrylobutadiene rubber	5-50
Stabilizer	1-5
Chemical foaming agent	3-20

Rigid foam. [Data from Ou, J.-W., **US Patent 5,238,966**, Aug. 24, 1993.]

Raw material	Concentration, parts
Kicker	0.2-5
Organic peroxide	0.5-3
Hollow Q cell or hollow phenol resin ball	10-100
Process aid (zinc fatty acid)	1-5

PVC foam containing promoter [Data from Lavallee, P. R., **EP2334718B1**, *PMC Organometallix Inc*, Feb. 17, 2016.]

Raw material	Concentration, parts
PVC K=57	100
Calcium stearate	0.7
165MP Wax	1
Oxidized polyethylene	0.2
Methyl tin stabilizer	2
High molecular weight acrylic process aid	8
Low molecular weight acrylic process aid	2
$CaCO_3$	5
Chemical blowing agent	0.85
Tin maleate	0.5
Titanium dioxide	4

Foamed article. [Data from Hori, T.; Ueki, K., **US Patent 5,162,380**, Nov. 10, 1992.]

Raw material	Concentration, parts
PVC containing epoxy groups	100
DOP	60
Calcium carbonate	80
Azodicarbonamide	25
Titanium dioxide	15
Ba/Zn stabilizer	3
Sodium dodecylbenzenesulfonate	1
Diluent	8

Rigid foam with superior surface characteristics. [Data from Kim, K.-U.; Kim, B.-C.; Hong, S.-M., **US Patent 4,956,396**, Sep. 11, 1990.]

Raw material	Concentration, parts
PVC	100
DOP	4
Impact modifier (MBS)	5
Process aid (Paraloid K-125)	5
Heat stabilizer (TM700R)	2
Lubricant (stearic acid)	0.5
Foaming agent (sodium bicarbonate)	0.75
Nucleating agent (boric acid)	0.75
*Relative tensile strength, %	150-300
*Relative compressive strength, %	200-300
Scratch resistance	superior

*Relative to the mechanical performance of a comparative example of foamed products which were not produced according to the invented formulation and technology.

Conditions of extrusion were found to be very essential for achieving the required product performance, and these are listed in the patent.

Thread masking foam. [Data from Peterson, F. C., **US Patent 4,856,954**, Aug. 15, 1989.]

Raw material	Concentration, wt%
PVC	45
Silicate filler	11
Pigment	0.5
Zinc octoate	2
Azodicarbonamide	1.5
Phthalate plasticizers	40

The composition is used to mask threaded area of the fastener to prevent paint sticking to it. After painting, the foam is thermally activated (by, for example, infrared heating) to expand and break paint which was sprayed on the masked surface.

Open-cell, hard foam. [Data from Waki, T.; Watanabe, T.; Suzuki, K., **US Patent 4,797,426**, Jan. 10, 1989.]

Raw material	A	B
	Concentration, parts	
PVC	100	100
Chlorinated polyethylene (Elaslen 301A)	10	10
Acrylic process aid (Methablen P-530)	5	10
Dibasic lead phosphite (getting obsolete)	2	
Dibutyltin dilaurate (Advastab T-12PJ)		1
Dibutyltin maleate (Advastab T-18J)		1
Anionic surfactant (Lipolan 1400)	2	2
Non-anionic surfactant (Liponox NC-2Y)	2	
Wax OP		1
Internal lubricant (Loxiol G-16)	1	2
Foaming agent (azodicarbonamide, AW-9)	1.5	1.5
Calcium carbonate (NS #100)	20	20
Appearance, cell shape, and permeability	good	good
Specific gravity, g/cm^3	0.28	

Irrigation pipe with foamed layer. [Data from Dorrn, C., **US Patent 4,577,998**, Mar. 25, 1986.]

Raw material	Concentration, parts
PVC (Corvic S67)	100
Tribasic lead sulfate (getting obsolete)	5
Diisooctyl phthalate	50
Calcium stearate	1
Acrylic process aid (Diakon APA)	5
Azodicarbonamide	1
p,p’-oxy-bis(benzenesulfonyl hydrazine) (blowing agent)	1
Titanium dioxide (pigment)	0.5
Carbon black (pigment)	0.02

Heat-foamable composition for transfer printing. [Data from Ishii, T.; Taratuni, T., **US Patent 4,482,598**, Nov. 13, 1984.]

Raw material	Concentration, parts
PVC	100
DOP	50
Epoxidized soybean oil	2
Calcium carbonate	10
Titanium dioxide	3
Zinc oxide	2
Azodicarbonamide	3

Printed foamable composition is transferred from release paper to the object being printed and then heat activated to obtain a decorative, three-dimensional print.

Crosslinked PVC foam. [Data from Sasajima, J.; Nagai, H.; Mogi, K.; Nojiri, A.; Shiina, N., **US Patent 4,434,251**, Feb. 28, 1984.]

Raw material	Concentration, parts
PVC (Zeon 103EP)	100
Di-n-decyl phthalate	70
Azodicarbonamide	15
Calcium carbonate	10
Trimethylol propane trimethylacrylate	5
Stearic acid	1
Octyltin mercaptide	3
Density, g/cm^3	0.08
Average cell diameter, μm	250
Discoloration	none

Crosslinking was done by electron beam irradiation immediately after the foam was expanded and was still at an elevated temperature.

Foamable plastisol. [Data from Mansolillo, R. D.; Kaminski, S. J., **US Patent 4,401,611**, Aug. 30, 1983.]

Raw material	Concentration, parts
PVC dispersion grade	600
PVC suspension grade	200
Mixed benzyl and alkyl phthalate esters	325
Alkyd secondary plasticizer	102
Limestone	100
Stabilizer	8
Blow mix composition (proportions):	
Azodicarbonamide	1000
Titanium dioxide	650
ZnO	375
Petroleum hydrocarbon	831
Wetting agent	30

Sheet backing for decorative covering material. [Data from Faust, K. J.; Woerner, D. C., **US Patent 4,175,154**, Nov. 20, 1979.]

Raw material	Concentration, parts
PVC dispersion resin	50
PVC suspension resin	50
Plasticizer	60
Pigment	7.5
Azodicarbonamide	2.5
Stabilizer/kicker	2.5

Extra-soft foam. [Data from Brunner, E.; Huber, A., **US Patent 4,070,107**, Mar. 14, 1978.]

Raw material	Concentration, parts
PVC (Lonza PE 704)	100
Phosphate plasticizer	50
DOP	50
Azodicarbonamide	20

Extra-soft foam. [Data from Brunner, E.; Huber, A., **US Patent 4,070,107**, Mar. 14, 1978.]

Raw material	Concentration, parts
Pigment	0.5
Liquid Ba/Cd stabilizer (obsolete)	6

Foam. [Data from Suzuki, K.; Miyazaki, H., **US Patent 4,014,7705**, Mar. 29, 1977.]

Raw material	Concentration, parts
PVC	60
EVA MW=1,000,000	20
EVA MW=500,000 (Evathlene 450)	20
PVAc (Evathlene 410)	60
Polyester-type plasticizer	25
Tribasic lead sulfate (close to be banned)	5
Antimony trioxide	5
Lead stearate (close to be banned)	1
Zinc borate	25
Aluminum hydroxide	15
Chlorinated paraffin (toxic)	10
Tensile strength, kg/mm^2	1.6
Elongation, %	390
Resistance, MΩ	40
Dielectric breakdown, min	9
Maximum temperature of conductor, ^{o}C	159

Container closure. [Data from Welch, B.; Wheeler, W., **US Patent 3,971,489**, July 27, 1976.]

Raw material	Concentration, parts
PVC (Geon G-92)	100
DOP	62
Precipitated calcium carbonate	20
Titanium dioxide	2
Ca/Zn stabilizer	1.4
Azodicarbonamide	0.8

4.8.4 CONCLUSIVE REMARKS

Major components of formulation include:

- PVC having low to high molecular weigh manufactured by all methods (suspension, emulsion, microsuspension, and mass), frequently used in combination (e.g., dispersion resin and suspension, or dispersion and blending resins)
- process aids (acrylic, lubricating, high molecular weight, ethylene vinyl acetate, zinc salts of fatty acids)
- lubricants (stearic acid, calcium stearate, oxidized polyethylene, polyethylene wax, paraffin wax, fatty acid esters, and butyl stearate; lubricants may affect the quality of foam; therefore their selection is important for product quality)
- plasticizer (a broad range of phthalates, phosphates, and chloroparaffins for flame retardant foamed products)
- blowing agent (mostly azodicarbonamide, but also sodium bicarbonate, benzenesulfonyl hydroxide, toluenesulfonyl hydrazine, and their combinations)
- kickers (MgO, ZnO, zinc octoate, and many other proprietary kickers)
- thermal stabilizer (selection of type and quantity of thermal stabilizer depends on process, for example, pressure molding is a long process (20-30 min) and therefore requires better stabilization; in other processes, usually a kicker alone is insufficient; several groups of stabilizers are used, such as, Ca/Zn, Ba/Zn, Na/Zn, and tin stabilizers; epoxidized oils and phosphites are used as costabilizers)

Several additives are used in addition to the main components, they include:

- fillers (most frequently calcium carbonate either coated or uncoated, but also, limestone, silicate, and wood flour have been used)
- titanium dioxide is a UV stabilizer used in products designed for outdoor applications
- impact modifiers (acrylic and MBS)
- diluents (regulate viscosity; mineral spirits and other petroleum hydrocarbons)
- nucleating agent (boric acid)
- surfactants and wetting agents
- aluminum hydroxide as a flame retardant

Major properties of foamed products include:

- cell size and uniformity, and cell structure (open or closed)
- product density
- mechanical performance
- outdoor performance
- thermal insulation properties

Some problems in production are formulation related, and these are as follows:

- surface roughness, blisters, and collapsed foam (undispersed foaming agent particles, poorly matched plastisol fusion rate and decomposition rate of foaming agent, or high ambient humidity)
- large irregular cells (plastisol being for too long time at fluid state)
- the high density of foam (too low concentration of foaming agent, too short residence time in the oven, or too slow decomposition rate of foaming agent for the fusion rate of plastisol)
- elephant skin (surface roughness appears near the end of the form; insufficient expansion at a temperature of this part of the mold)
- sink marks (more blowing agent needed)
- plateout (less blowing agent should be used)

4.9 GEL & SEALANT FORMULATIONS

Sealant applications are major commercial products, which fall into two categories: PVC plastisols which do not have reactive components and PVC plastisols combined with blocked isocyanates or isocyanurates. The first category of sealants is the most popular as an underbody sealant, whereas the second category includes construction and general purpose sealants. PVC gels are used occasionally as electrolytes, vibration reducing materials, and the like.

4.9.1 FORMULATION PROPOSED BY THE RAW MATERIAL SUPPLIER

Underbody sealant and coating. [Data from **PVC/acrylics plastisols**. *Solvay*.]

Raw material	Concentration, parts
PVC (Vinnofil SPT Premium)	25
Plasticizer(s)	36
Precipitated calcium carbonate (Socal 311, 312, U1S1, or 312V)	20
Ground calcium carbonate	12
Other additives including adhesion promoter, CaO, ZnO, and hydrocarbon oil for viscosity control	7

4.9.2 PATENTED INVENTIONS

Body sealer. [Data from Nakayama, K.; Ohno, H.; Minamihori, T., **US Patent 7,332,539**, Feb. 19, 2008.]

Raw material	PVC	Acrylic
	Concentration, parts	
Particulate acrylic resin (F345 from Zeon Kasei Co.)		10
PVC (PSH180 from Kaneka Co.)	20	
Calcium carbonate	49	53
Diisononyl phthalate	30	25
Blocked polyurethane prepolymer		10
Latent curing agent (Fujicure FXE-1000 from Fuji Kasei)		1
Calcium oxide	1	1

Unlike PVC, which requires high temperatures (180°C and higher), acrylic body sealer can be cured at 100°C. Both formulations have excellent storage stability and low-temperature flexibility.

Seam seal and lining adhesive with excellent adhesion. [Data from Butschbacher, G., **US Patent 7,163,976**, Jan. 16, 2007.]

Raw material	Concentration, wt%
E-PVC (Vestolit P 1353 K)	13
VC/VAc copolymer (Vinnolit C 14/60 V)	10
VC/VAc copolymer (Lacovyl PA 1384)	2
E-PVC (Vestolit E 7031)	13
Diisononyl phthalate	36.4
Hydrocarbon (Shellsol D 70)	4.6
Calcium oxide (Schafer, Super 40)	3.5
Zinc oxide (zinc white resin seal)	0.4
Pigment (carbon black paste Tack DINP 25/V)	0.2
PVC hollow beads (Dualite M 6001 AE)	1.1
Formulated polyaminoamide (Euretek 507)	1.6
Calcium carbonate (Hydrocarb OG)	2.5
Precipitated calcium carbonate (Winnofil SPT)	2
Silica (Aerosil 200)	0.4
Magnesium oxide (extra light)	1
Sucrose	10

Separators for winding-type lithium secondary batteries. [Data from Noh, H.-G., **US Patent 6,924,065**, Aug. 2, 2005.]

Raw material	Concentration, parts
PVC	1
Polyvinylidenefluoride	2
N-methylpyrrolidone	50
Ethylene carbonate	12
Fume silica	1

The resultant composition was coated on antiadhesive film, dried, extracted with methanol to remove traces of solvents. The film produced was used as a gel separator in lithium batteries.

Self-levelling plastisol. [Data from Rinka, R. A.; Hubert, J. F., **US Patent 6,429,244**, Aug. 6, 2002.]

Raw material	Concentration, parts
PVC (KV-2 from Formosa Plastics)	300
PVC (Vinycel 10x122 from Shawnee Chemical)	150
Diisodecyl phthalate	575
Coarse ground calcium carbonate (Q-325)	1050
Hydrogenated castor wax (Flowtone R)	105
Calcium oxide	37.5
Proprietary polyamide (Surfac 555 from Shell)	22.5
Mineral spirits	75

Light-weight underbody compound. [Data from Malbom, L.; Lysell, L., **US Patent 5,629,364**, May 13, 1997.]

Raw material	Concentration, parts
PVC copolymer (5% VAc, Vinnol E5/65L)	213
PVC copolymer (8% VAc, Vinnol C8/62 V)	60
Diisononyl phthalate	390
Filler (calcium carbonate, Durcal 5)	200
Filler (calcium carbonate, Socal P2)	123
Viscosity regulator (Aerosil 200)	10
Tin stabilizer (dibutyltin carboxylate, Irgastab T9)	4

Automotive underbody sealant. [Data from Buess, P, Caers, R F, Colle, K S, Godwin, A, Saleh, R Y, Stanat, J E R, Less, D, **European Patent EP2268727**, Jan. 5, 2011, *ExxonMobil Chemical Patents Inc.*]

Raw material	Concentration, parts
PVC copolymer	100
Polyol ester plasticizer (this invention)	50
DINP	50
Calcium carbonate	100
Other additives	20

Sealer. [Data from Miyataka, K.; Nakayama, T., **US Patent 5,338,788**, Aug. 16., 1994.]

Raw material	Concentration, parts
PVC (Zeon 121)	200
PVC crosslinker (Vinica P-100)	100
Diisononyl phthalate	400
Surface treated calcium carbonate	270
Calcium carbonate	300
1,3,5-triglycidyl isocyanurate	15
Other additives	60

This sealer has several exceptional properties, such as no cracking of topcoat paint, excellent elongation, storage stability, and excellent adhesion.

Rubbery blend with low permanent compression set. [Data from Ngoc, H. D.; Duval, G. P. R., **US Patent 5,362,787**, Nov. 8, 1994.]

Raw material	Concentration, parts
PVC (K=71)	100
DOP	50
Stabilizer	3
Powdered, crosslinked nitrile rubber	30

Compression set is a typical feature of PVC sealants because gelled PVC has plastic properties (no rubbery behavior). Addition of crosslinked nitrile rubber adds rubbery particles which can reduce compression set.

Sealant made from PVC plastisol. [Data from Palermo, A. C.; Schimmel, K. F.; Chau, M. M., **US Patent 5,248,562**, Sep. 28, 1993.]

Raw material	Concentration, parts
PVC (Vestolit E-7012)	15.9
PVC (Oxy 567)	5.6
VC/VAc (95/5) copolymer (Oxy 6338)	2.8
Calcium carbonate (Snowflake)	20.6
Stearic acid coated calcium carbonate (Multiflex SC)	17.5
Calcium oxide	8.3
Fume silica (Cabosil TS-720)	0.7

Sealant made from PVC plastisol. [Data from Palermo, A. C.; Schimmel, K. F.; Chau, M. M., **US Patent 5,248,562**, Sep. 28, 1993.]

Raw material	Concentration, parts
DIDP	25.6
Copolymer E (25% solution in DIDP of reaction product of 1-decene and maleic anhydride)	7.4
Copolymer F (11.4 wt% solution in DIDP of Chemigum P-83, copolymer of 33% acrylonitrile, 63% butadiene, 4% divinyl benzene)	19.1
Organophosphite (Synpron 431)	1.2

One of the features of this formulation is a broad use of different fillers in combination to regulate rheological properties required by the sealant.

PVC plastisol with blocked polyisocyanurate. [Data from Nakata, Y.; Tomoyasu, H., **US Patent 5,204,391**, Apr. 20, 1993.]

Raw material	Concentration, parts
PVC (PSH-10)	50
PVC (PBM-10)	250
DOP	100
Hexamethyl diisocyanate blocked with phenol	25
Surface treated calcium carbonate (Hakuenka CCR)	50
Limestone powder (Whiton B)	120
Calcium oxide	5

Similar to the previous formulation, the rheological properties are regulated with extensive use of fillers. Here, a typical combination of coarse, untreated limestone and special surface-treated calcium carbonate is used. This formulation also differs from the previous one in that it includes blocked polyisocyanurate which can react at an elevated temperature after phenol blocking is removed by dissociation at high temperature.

Electrophoretic coatable sealant composition. [Data from Gerace, J. M.; Gerace, M. J., **US Patent 5,143,650**, Sep. 1, 1992.]

Raw material	Concentration, wt%
PVC dispersion resin (Vestolit E 7031)	19
Copolymer of VC with dibutyl maleate (Pliovic MC-85)	8
Diisodecyl phthalate	28
Epoxidized soybean oil	2
Vinyl acetate ethylene copolymer (Vynathene EY80031)	13
Adhesion promoter (3-methacroylpropyl trimethoxy silane)	0.3
Epoxy resin (Heloxy 8005)	2
Calcium organic thixotropic agent (Irgogel 903)	0.5
Methacrylate ester adhesion promoter (Chemlink 9010)	4.5
Calcium carbonate filler (Cal L)	8.04
Hydrophobic fume silica (Cab-O-Sil TS-720)	4.15
Calcium oxide	2
Anionic wetting agent (BYK W-960)	0.16
Modified polyamide hardening agent (Hardener HY 940)	3
Cumene hydroperoxide	0.08
Tribasic lead sulfate (now getting obsolete)	1
Hydroquinone monomethyl ether	0.02
Tetrahydrophthalic anhydride adhesion promoter	0.3
Carbon black pigment	0.05
Titanium dioxide	0.05
Carbon black (Ketjenblack EC-3001)	3.85

Sealant. [Data from Huynh-Tran, T.-C., **US Patent 5,130,200**, Jul. 14, 1992.]

Raw material	Concentration, wt%
PVC homopolymer	8
VC/VAc copolymer (5% VAc)	10
Epoxy resin (Bisphenol A epoxy resin diluted with 15 wt% of C12-C14 aliphatic glycidyl ether)	3
Maleic anhydride	1.71

Sealant. [Data from Huynh-Tran, T.-C., **US Patent 5,130,200**, Jul. 14, 1992.]

Raw material	Concentration, wt%
Polyadipic polyanhydride	0.3
Succinimide	5
Diisodecyl phthalate	28.84
Calcium oxide	2.82
Calcium carbonate	40.33

Exceptional properties of this sealant include excellent bond shear adhesion (20.4 kg/cm^2) after 120^{o}C/30 min cure and stable viscosity (because of the use of succinimide).

Low-temperature insulating material. [Data from Nakashita, T.; Mitsuba, A.; Touji, D.; Tomiga, I.; Nakashio, Y.; Nagase, T., **US Patent 5,077,336**, Dec. 31, 1991.]

Raw material	Concentration, parts
PVC	10
Dibutyl phthalate	40
Di-(2-ethylhexyl) phthalate	40
Di-(2-ethylhexyl) adipate	40
Glycerol monooleate	12
Polyvinyl alcohol	3
Borate glass powder	0.3
Water	100

Hot-applied plastisol composition. [Data from Gerace, M. J.; Gerace, J. M., **US Patent 5,039,768**, Aug. 13, 1991.]

Raw material	Concentration, wt%
PVC dispersion resin (Vestolit E 7011)	19
PVC blending resin (Pliovic MC-85)	8
Diisodecyl phthalate	8
Vinyl acetate ethylene copolymer (Vynathene EY80031)	13
Adhesion promoter (3-methacroylpropyl trimethoxy silane, Z 6030)	0.3
Elastomeric epoxy resin (Heloxy 8005)	2
Adhesion promoter (methacrylate ether, Chemlink 9010)	4.5

Hot-applied plastisol composition. [Data from Gerace, M. J.; Gerace, J. M., **US Patent 5,039,768**, Aug. 13, 1991.]

Raw material	Concentration, wt%
Precipitated calcium carbonate (Hakuenka CC)	16.80
Polyaminoamide (Euretek 580)	3
Calcium oxide	2
Cumene hydroperoxide	0.08
Tribasic lead sulfate (now becoming obsolete)	1
Hydroquinone monomethyl ether	0.02
Cis-1,2,3,6-tetrahydrophthalate anhydride	0.3
Polypropylene glycol dibenzoate (Benzoflex 400)	10
Trioctyl trimellitate	10
Polyadipic acid ester (Plasthall P-670)	2

Blocked polyisocyanurate-containing plastisol. [Data from Nakata, Y.; Kunishiga, T., **US Patent 4,983,655**, Jan. 8, 1991.]

Raw material	Concentration, parts
PVC (Kaneka PCH-12Z)	60
PVC (Zeon G51)	40
DOP	30
Blocked isocyanate compound (TDI blocked with styrenated phenol)	50
Surface-treated curing agent (Nobacure 3721)	2.4
Surface-treated calcium carbonate (Neolite SP)	25
Hollow glass powder (Glassballoon Z-37)	6
Kerosine	15
Calcium oxide (QCX)	10

4.9.3 CONCLUSIVE REMARKS

The major formulation components include:

- plasticizers (a large number of different plasticizers are in use, such as phthalates from dibutyl phthalate to diisodecyl phthalate, benzoates, adipates, trimellitates, and polymeric plasticizer; selection depends on the expected durability of sealant which can be affected by its loss due to volatility; concentrations are high, usually 100 to 140 phr)

- fillers (fillers here play a very specific role of rheological additives which help to obtain non-sag properties of sealant (both automotive and construction); the most frequent is a combination of precipitated coated calcium carbonate of very small particle size and ground calcium carbonate; there are also other fillers used to support the idea of thixotroping by a combination of two fillers, these include fumed silica, and special types of carbon black (Ketjenblack) used to increase thixotropic properties, and silica, PVC hollow beads, hollow glass beads on the side of general filler with the last two meant to lower density)
- hydrocarbons such as hydrocarbon oil, mineral spirits or kerosene are used to reduce viscosity in cheaper products
- an adhesion promoter (silanes, tetrahydrophthalic anhydride, and methacrylate ester) are frequently necessary to maintain good adhesion to metal

Less commonly used additives include:

- thermal stabilizers or oxides of stabilizing metals (Ca and Zn)
- various blending resins, including combinations of different grades of PVC, acrylic resin, VC/VAc copolymer, ethylene vinyl acetate copolymer, crosslinked nitrile rubber, epoxy resin, and polyvinylidene fluoride. Polyurethane has a special place here because it is used to obtain elastomeric properties required in construction and some automotive sealants. Nonyl phenol-blocked and isocyanate (or polyisocyanurate) combination is added to PVC plastisol. These sealants have a relatively stable viscosity

Most important properties include:

- thixotropic properties (most sealants must have non-sag properties to be applied either to an underbody (automotive) or on vertical surfaces (construction))
- self-leveling properties (some sealants are cured after application, and they are easier to apply if they do not have strong thixotropic properties),
- stability of rheological properties (changes in viscosity affect product usability)
- cure rate and reliability of cure
- surface tack (tacky, or not well-cured sealants, will attract dust)

Production and storage problems include several formulation related cases:

- loss of thixotropic properties (wrong proportions of thixotropic and general fillers; instability of polyurethane),
- increase in viscosity (instability of resin due to the selection of catalyst or incomplete blocking)
- inferior mechanical performance (incomplete cure due to restrictions in moisture intake (moisture required to unblock polyurethane) or insufficient catalysis)
- dirt pickup (insufficient cure, excessive plasticizer)
- UV degradation (stabilization, insufficient cure)

4.10 INJECTION MOLDING

4.10.1 GENERAL

4.10.1.1 Formulations proposed by the raw material suppliers

Ca/Zn stabilization. [Data from **Waxes for PVC Lubrication**. *Clariant*, 2013.]

Raw material	Concentration, parts
S-PVC (K=57)	100
Ca/Zn stabilizer	2.8
PMMA processing aid	1
Licowax E/Licocare SBW 11 TP	0.9

Lead stabilization. [Data from **Waxes for PVC Lubrication**. *Clariant*, 2013.]

Raw material	Concentration, parts
S-PVC (K=60)	100
Tribasic lead sulfate	2.5
Dibasic lead stearate	0.6
Neutral lead stearate	0.3
Calcium stearate	0.4
Glycerol monostearate	0.5
Licowax E/Licolub WM 31	0.5

Tin stabilization. [Data from **Waxes for PVC Lubrication**. *Clariant*, 2013.]

Raw material	Concentration, parts
S-PVC (K=60)	100
Sn stabilizer containing sulfur	2
Impact modifier	2
PMMA processing aid	1
Glycerol monostearate	1
Licowax E/Licolub WM 31/Licocare SBW 11 TP	0.5

4.10.1.2 Patented inventions

Ternary alloys having high heat distortion temperature. [Data from Soby, L. M.; Lehr, M. H.; Dickens, E. D.; Rajagopalan, M.; Greenlee, W. S., **US Patent 5,354,812**, Oct. 11, 1994.]

Raw material	Concentration, parts
PVC	30
CPVC	10
Imidized methylmethacrylate (HT510)	60
Tin stabilizer (Thermolite 31)	2
Acrylic process aid (K120N)	1.5
Oxidized polyethylene lubricant (AC629A)	0.25
Heat distortion temperature, °C	103.5
Heat distortion temperature for PVC alone, °C	72

Chlorinated PVC blends. [Data from Greenlee, W. S.; Kinson, P. L.; Rajagopalan, M., **US Patent 5,274,043**, Dec. 28, 1993.]

Raw material	Concentration, parts
CPVC (68 wt% chlorine)	56
PVC	35
Impact modifier	12
Tin mercaptide stabilizer	1.8
Lubricant	3
Tensile strength, MPa	51.62
Notch Izod, Nm/m	246
Anneal heat distortion temperature, °C	83.9
Spiral flow, cm	42.4

Blends with ionomers. [Data from Parker, H.-Y., **US Patent 5,252,667**, Oct. 12, 1993.]

Raw material	PVC	Blend
	Concentration, parts	
PVC (K=60)	100	100
Methylmethacrylate (90)/butyl acrylate (10)/methacrylic acid (1.72) Na^+ ionomer		14
Heat stabilizer (mono/dimethyltin bis-(2-ethylhexyl thioglycollate)	2	2
Lubricant (glycerol monostearate)	2.7	2.7
Lubricant (polyethylene wax, AC 629A)	0.3	0.3
Acrylic impact modifier (KM 175)	15	15
Process aid (K 175)	1	1
Titanium dioxide	1.5	1.5
Glass transition temperature, °C	78.1	79.2
Tensile yield stress, MPa	38.5	42.1
Tensile modulus, GPa	1.81	2.10
Notched Izod, J/m	1249	1142

Flow improvement in blends modified for impact strength. [Data from Foelsch, K. J.; Frank, K.; Jung, K.-S., **US Patent 5,185,404**, Feb.9, 1993.]

Raw material	Control	Modified
	Concentration, parts	
PVC (Solvic 250)	50	50
ABS (Blendex 703)	50	50
Pigment (Kronos CL 230)	3	3
Lubricant (Loxiol)	4	4
Lubricant (Loxiol G70S)	0.8	0.8
Irgastab T 22 M	2	2
Rheology improver (methylmethacrylate/n-butyl methacrylate=80/20)		5
MFI, g/10 min.	293	3.94
Viscosity, Pas	4915	3161
Spiral flow length, cm	58	73

PVC blends. [Data from Greenlee, W. S.; Kinson, P. L.; Kline, S. A.; Rajagopalan, M.; Daniels, C. A., **US Patent 5,143,975**, Sep. 1 1992.]

Raw material	Control	Blend
	Concentration, parts	
PVC (inherent viscosity=0.46)	100	80
PVC (inherent viscosity=0.92)		20
Impact modifier	8	8
Lubricant	3	3
Tin stabilizer	2	2
Process aid	2	2
Heat deflection temperature, °C	70.5	68.5
Vicat B, °C	80.5	83.5
Spiral flow, inch	39.5	29.5
Low shear viscosity, P	5098	7803

Special PVC for injection molding. [Data from Bieringer, H.; Engler, M.; Holtrup, W., **US Patent 4,588,791**, May 13, 1986.]

Raw material	Concentration, parts
PVC	100
Ba/Cd stabilizer (obsolete)	2.5

Special PVC was produced by suspension polymerization at two or more temperatures in the presence of an oil-soluble catalyst and other additives. The technology described in this invention can produce PVC having reduced melt viscosity. For two polymers processed according to the above formulation, spiral flow length was 54 cm for new technology polymer compared to 38.5 cm for a polymer having the same K number (58.5) but produced by conventional technology.

Nailable PVC material. [Data from Burkey, D. J.; Rosenau, C. M., **US Patent 4,105,717**, Aug. 8, 1978.]

Raw material	Concentration, parts
PVC	100
Chlorinated polyethylene (CPE 36-14)	20
Thermal stabilizer (Thermolite 31)	5
Acrylic process aid (K-120)	2
Polyethylene wax (OP)	2
Styrene acrylonitrile copolymer (RMDA-4420)	25
Styrene butadiene copolymer (Kraton 3204)	10
Titanium dioxide	0.66
Melt flow index at 190°C, g/min	31.6
Nailability	good

Rigid PVC. [Data from Eilers, K. L.; Kopacki, A. F., **US Patent 3,983,186**, Sept. 28, 1976.]

Raw material	Concentration, parts
PVC	100
Organotin mercaptide (Thermolite 31)	2
Calcium stearate	2
Low molecular weight polyethylene wax	0.1
Titanium dioxide	1
Process aid	1

This formulation permits one to obtain parts having high gloss and smoothness. The technology is discussed in detail.

High-impact-resistant high-flowability PVC (polyvinyl chloride) injection molding material [Data from **CN107082977A**, Aug. 22, 2017.]

Raw material	Concentration, parts
PVC resin (SG8) polymerization degree 700-900	90
ACR-g-VC resin (SG5)	10
Impact modifier (ACR, CPE, or MBS)	5
Composite stabilizer	3.5
Internal lubricant (e.g., calcium stearate)	0.5

High-impact-resistant high-flowability PVC (polyvinyl chloride) injection molding material [Data from **CN107082977A**, Aug. 22, 2017.]

Raw material	Concentration, parts
Oxidized polyethylene wax	0.5
Calcium carbonate (nano size)	5

4.10.1.3 Formulations found in the open literature

The plasticizing effects of cardanol acetate and epoxidized cardanol acetate compared favorably with di-(2-ethylhexyl) and diisononyl phthalates in semi-rigid formulations.

Semi-rigid PVC with plasticizers based on natural products. [Data from Chen, J.; Liu, Z.; Nie, X.; Zhou, Y.; Jian, J.; Murray, R. E., *J. Polym. Res.*, **25**, 128, 2018.]

Raw material	Concentration, parts
PVC (DG-1000 K)	100
Cardanol acetate or epoxidized cardanol acetate	25
Calcium stearate	1.5
Zinc stearate	0.5

4.10.2 COUPLINGS AND FITTINGS

4.10.2.1 Formulations proposed by the raw material suppliers

Fittings. [Data from **Thermolite 161**. *Arkema*.]

Raw material	Concentration, parts
PVC (K=58)	100
Thermolite 161 (methyltin mercaptide)	1.5-2
Calcium stearate	1-1.2
Paraffin wax (melting point=74°C)	0.8-1.2
Plastistrength 550	1-2
Durastrength 200	2-3
Calcium carbonate (particle size=0.8 μm)	3-5
Titanium dioxide	0-1

Fittings. [Data from **Mark 1993**. Technical data sheet. *Chemtura Corp*.]

Raw material	Concentration, parts
Low molecular weight PVC	100
Titanium dioxide	1
Calcium carbonate (small particle size)	4
Marklube L-100A	1.5
Marklube L-107	0.5
Highly oxidized polyethylene wax	0.2
Mark 1993 (methyltin reverse ester mercaptide)	1.5

4.10.2.2 Formulations found in the open literature

Pipe fittings. [Data from Carroll, W. F., Johnson, R. W., Moore, S. S., Paradis, R. A., **Applied Plastics Engineering Handbook**, Chapter 5. Poly(vinyl chloride), *Elsevier*, 2011, p. 61-76.]

Raw material	Concentration, parts
PVC (K=55-60)	100
Stabilizer	high tin
Filler	0-5
TiO_2	0-2
Processing aid	0-3
Calcium stearate	0.8-2
Paraffin wax	1-2
Oxidized polyethylene	0-0.4

Fittings. [Data from Fisch, M. H.; Bacaloglu, R.; Biesiada, K.; Brecker, L. R., *J. Vinyl Additive Technol.*, **5**, 1, 45-51, 1999.]

Raw material	Concentration, parts
PVC	100
Calcium carbonate	5
Titanium dioxide	1
Calcium stearate	1
Epoxidized soybean oil	1
Impact modifier	1.5
Methyltin thioglycollate stabilizer	1

Fittings with organic-based stabilizer, OBS 200 series. [Data from Edser, C., *Plastics Additives Compounding*, **3**, 11, 26-30, 2001.]

Raw materials	Concentration, parts
PVC (suspension, K=58-67)	100
OBS 300 series (Chemtura)	3.5-5
Impact modifier	0-1
Process aid	0-1
Filler	3.5-5
Pigment	quantum satis

4.10.3 TOYS

4.10.3.1 Formulation proposed by the raw material supplier

Toys (closed mold). [Data from **Eastman TXIB. Plasticizer in toys**. Publication L-225. *Eastman*. December 1997.]

Raw material	Concentration, parts
PVC dispersion resin	50
PVC blending resin	50
DOP	81
Eastman TXIB (plasticizer)	9
Epoxidized soybean oil	5
Stabilizer	3

4.10.3.2 Patented invention

Toys. [Data from Becker, H G, Grass, M, Huber, A, **European Patent EP2643399**, Oct. 2, 2013, *Evonik Oxeno GmbH*.]

Raw materials	Concentration, parts
Vestolit P1352 K	100
Hexamol DINCH	70
Calcilit 8 G	100
Kronos 2220	7
Isopropanol	3
Uniform AZ Ultra 1035	2.5
Zinc oxide	1.5

4.10.4 OTHER PRODUCTS

4.10.4.1 Formulations found in the open literature

High flow compound. [Data from Stevenson, J. C.; Fazey, A. C., *J. Vinyl Additive Technol.*, **3**, 2, 118-125, 1997.]

Raw material	Concentration, parts
PVC (=50-55)	100
Tin stabilizer	2
Glycerol monostearate (internal lubricant)	2.7
Polyethylene wax (external lubricant)	0.3
Acrylic process aid	1-2
Lubricating acrylic process aid	1-1.5
Impact modifier	10-12
Titanium dioxide	1-12

High heat deflection temperature. [Data from Zerafati, S., *J. Vinyl Additive Technol.*, **4**, 1, 35-38, 1998.]

Raw material	Concentration, parts
PVC (K=55)	100
Butyltin stabilizer	2.0
Paraffin wax	1.5
Calcium stearate	1.5
Methyl methacrylate-butadiene-styrene, impact modifier	20
Poly(α-methylstyrene-styrene-acrylonitrile), HDT additive	20
Oxidized PE	0.3
Titanium dioxide	4.5

Poly(α-methylstyrene-styrene-acrylonitrile) has a higher glass transition temperature (130°C) than PVC, and it is compatible with PVC. The more HDT additive added, the higher the deflection temperature of the blend. Optimization of HDT additive concentration and concentration of impact modifier helps to improve both properties.

Parts with high impact and high stiffness. [Data from Wiebking, H. E., *J. Vinyl Additive Technol.*, **2**, 3, 187-189, 1996.]

Raw material	Concentration, parts
PVC resin (K=66)	100
Stabilizer (methyltin)	1.5
Process aid	1.0
Calcium stearate	1.2
Wax	1.0
PE wax	0.2
Impact modifier (modified acrylic)	20
Ultrafine talc (particle size = 0.9 μm, e.g., UltraTalc)	15-20

The reported study demonstrates that it is possible to increase Izod impact strength without reducing stiffness. This can be done by the use of high levels of acrylic impact modifier in combination with ultrafine talc. The modifier imparts impact strength, while the talc maintains a stiffness that would have been lost if the impact modifier was used alone.

4.10.4.2 Patented inventions

High flow compound. [Data from Shakir, S, Lee, S, **European Patent EP2310451**, Apr. 20, 2011, *PolyOne Corporation.*]

Raw material	Concentration, parts
Oxyvinyl 185	100
Mark 2294	2.2
Weston EHDP phosphite	0.75
Kyowa Alcamizer MHT-PD (hydrotalcite)	0.5
Plastistrength 550 (process aid)	1.5
Polaroid K-175 (process aid)	0.75
Calcium stearate	1
Paraffin wax	0.85
Polyethylene wax (OPE-ACE-629-A)	0.75
Omyacarb UFT	5
Tiona RCL-88	1.75

Products from recycled carpet waste. [Data from Riccirdelli, T. E.; King, M. H.; Slater, M. P.; Raposo, S. F., **US Patent 6,723,424**, Apr. 20, 2004.]

Raw material	Concentration, wt%
Vinyl-backed carpet containing 25% nylon fiber, and 70% backing, which contains 30% PVC, 15% nylon fiber, and 55% filler	10-75
Flexible PVC	25-90
Plasticizer (DOP)	q. s.

The invention describes the production of molded articles from waste such as flexible tile. The method of manufacture is well illustrated and described.

Wood fiber composite. [Data from Seethamraju, K. V.; Heikkila, K. E.; Deaner, M. J., **US Patent 6,210,792**, Apr. 3, 2001.]

Raw material	Concentration, parts
PVC (Geon 427)	100
Methyltin mercaptide (Advastab TM 181)	1
Lubricant (Loxiol VGE 1884)	1.7
Oxidized polyethylene	0.4
Saw dust	20.62
Styrene maleic anhydride copolymer (Dylark 332)	10.31

Plastic tile. [Data from Wang, C.-H.; Wang, Y.-C., **US Patent 6,132,846**, Oct. 27, 2000.]

Raw material	Concentration, wt%
PVC	23.2
ABS	34.8
Diatomite	10
Barium sulfate	8
Organotin stabilizer	6
Antimony trioxide	5
Dihexyl phthalate	10
Pigment	1

Plastisol earpieces for acoustical control. [Data from Tutor, M. S.; Green, R. T., **US Patent 6,129,175**, Oct. 10, 2000.]

Raw material	Concentration, parts
PVC	100
DOA	400
DOP	70
Epoxidized soybean oil	10
Ca/Zn stabilizer	10
Pigment	q. s.

Non-flammable composition. [Data from Mishima, I.; Ikeda, M.; Hosoi, H., **US Patent 5,466,750**, Nov. 14, 1995.]

Raw material	Concentration, parts
Copolymer of acrylonitrile (12), butyl acrylate (60), styrene (18), and α-methylstyrene (10)	5
Copolymer of α-methylstyrene (72) and acrylonitrile (28)	35
Copolymer of polybutadiene (65), styrene (7), and methylmethacrylate (28)	15
Post-chlorinated PVC	50
Dibutyltin maleate	2
Mercaptotin acid stabilizer	1
Glycerin tristearate	1
Polyethylene wax	1

Insect control device. [Data from Rose, W. B.; Arther, R. G., **US Patent 5,018,481**, May 28, 1991.]

Raw material	Concentration, parts
PVC	90.7
Epoxidized soybean oil	0.91
Diethyl phthalate	13.6
Coumaphos	34.7

Use of this device reduced the number of flies in South Texas by 50% and in Georgia by 84.3%.

Boots for automobiles. [Data from Ohta, S.; Takimoto, M.; Yamazaki, Y.; Mizutani, H., **US Patent 4,902,545**, Feb. 20, 1990.]

Raw material	Concentration, parts
Crosslinked PVC (polymerization degree=1800)	60
Non-crosslinked PVC (polymerization degree=700)	40
Diisononyl phthalate	120
Ba/Zn stabilizer	2

4.10.5 CONCLUSIVE REMARKS

A large variety of products are produced by injection molding, with each application having special needs, but several commonalities can be found, such as

- PVC has low to moderate molecular weight (mostly low molecular weight to improve flow rate and distance)
- mercaptotin stabilizers are used in most applications (high shear rates require fast reacting stabilizer)
- acrylic process aid is most frequently needed to improve process efficiency
- proper lubrication also improves quality and production cycle (the following lubricants are the most commonly used: PE wax, oxidized PE, glycerol monostearate)

Some specific additives are also used, as follows:

- various properties are modified with a large number of blended polymers, such as CPVC, imidized PMMA, methylmethacrylate butyl acrylate methacrylic acid ionomer, ABS, methylmethacrylate n-butyl methacrylate copolymer, chlorinated PE, styrene-acrylonitrile copolymer, styrene butadiene copolymer, methylstyrene-styrene-acrylonitrile copolymer, styrene-maleic anhydride copolymer. These polymers improve mechanical properties, impact strength, change rheological properties, and increase heat deflection temperature
- plasticizers are used in some formulations which require flexible products (e.g., toys); they include phthalates, TXIB, and adipates
- fillers are less frequently used because they affect flow properties. Sometimes smaller quantities of calcium carbonate are used to lower the price of the product or filler is used for specific purposes (e.g., talc was used to improve stiffness)
- other additives include impact modifier (acrylic or MBS) and melt strength controlling additive

The following are the most critical properties of injection molded materials and material requirements for the injection molding process:

- aesthetics (depends on formulation, properties of mold surface and surface of the molded product and their adhesion and processing parameters; gloss changes and lack of gloss uniformity, color changes, and colored particulates, either from contamination or degradation)
- mechanical performance is affected by formulation and conditions of cooling (crystallization)
- repeatable dimensions (can be changed by swelling after removal from the mold, or by deformation)
- rheological properties which influence aesthetics and production rate
- release properties influence production rate and cooling energy and time

The following are the most frequently encountered production problems which are related to formulation:

- incompletely filled parts (change in material composition or rheology),
- sink marks after demolding (insufficient blowing agent, the composition has too high shrinkage)
- burnt streaks (too much regrind, inadequate stabilization, contamination, the material contains too much moisture)
- dark spots (contaminations, dye incompatibility, contamination with burnt material)
- gloss variation (filler and pigments may cause differences; type and quantity should be investigated)
- color change near weld line (too much pigment, pigments with spherical particles should be used)
- stress whitening (too high crystallinity of material, increased molecular weight, and its narrower distribution should help)
- deformation during demolding (release agent should be used)
- delamination or flaking (too high moisture in resin or additives, impurities, incompatible dye)

Further information on this subject can be found in the following books:

1. Goodship, V., **Arburg Practical Guide to Injection Moulding**, *Rapra*, Shawbury, 2004.
2. Goodship, V.; Love, J. C., **Multi-material Injection Moulding**, *Rapra*, Shawbury, 2002.
3. Frenkel, D.; Zawistowski, H., **Hot Runners in Injection Moulds**, *Rapra*, Shawbury, 2001.
4. Fischer, J. M., **Handbook of Molded Part Shrinkage and Warpage**, *William Andrew Publishing*, Norwich, 2003.

4.11 JOINING AND ASSEMBLY

Many parts manufactured from PVC are joined or assembled using specially designed structural elements, some of which are presented below. Also, special adhesive formulations are available which are given below.

4.11.1 Patented inventions

Bending PVC profiles using laser and PLC controlling system. [Data from Turanjanin, U, **European Patent EP 2608946**, Jul. 3, 2013.]

PVC profile bending using laser and PLC controlling system is a part of the arched PVC joinery, where the bending of the PVC profiles is completely automatized thus removing any possible human error caused by operating the machine manually.

Door with wooden and plastic components. [Data from Ellingson, R. T., **US Patent 7,160,601**, Jan. 9, 2007.]

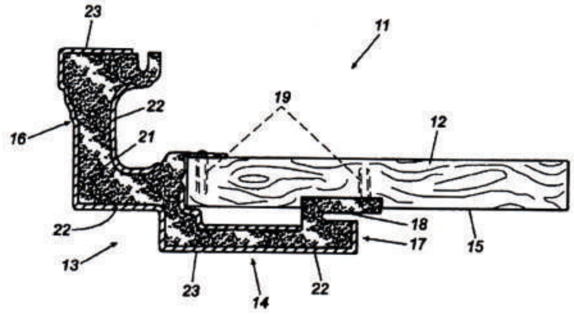

Figure 4.1. Mounting wooden jamb using plastic bricks. [Adapted from Ellingson, R. T., **US Patent 7,160,601**, Jan. 9, 2007.]

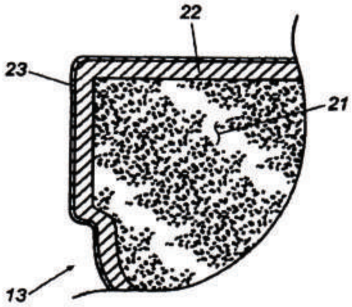

Figure 4.2. Structure of plastic brick. See text for explanations. [Adapted from Ellingson, R. T., **US Patent 7,160,601**, Jan. 9, 2007.]

Figure 4.1 shows the connection between a wooden jamb (12) assembly and plastic brick (14) manufactured from the composite. Figure 4.2 shows the structure of plastic brick (14) which is composed of cellular PVC core (21), SAN stabilizing layer (22), and non-cellular PVC wear layer (23). This combination was found to be very resilient and scratch-resistant.

Joining mechanism of PVC pipe. [Data from Allouche, E., **US Patent 6,918,618**, Jul. 19, 2005.]

As shown in Figure 4.3, a PVC-pipe, axially-tensioned joint (10) functions to join the first PVC pipe (12) and a second PVC pipe (14). Figure 4.4 shows that the first PVC pipe (12) has an axial direction AD_S, a spigot end (16) and a first axial opening (18) at the spigot end (16). The spigot end (16) has an outside diameter OD_S and an outer surface (20). There is a circumferential groove (22) in and

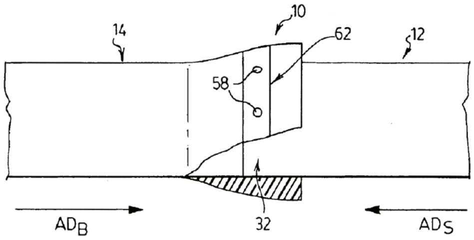

Figure 4.3. General view of joint of two PVC pipes. [Adapted from Allouche, E., **US Patent 6,918,618**, Jul. 19, 2005.]

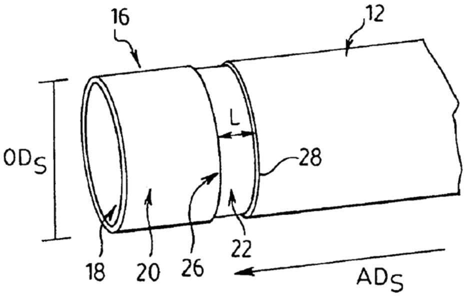

Figure 4.4. The structure of the first pipe to be joined. For numerical symbols see text. [Adapted from Allouche, E., **US Patent 6,918,618**, Jul. 19, 2005.]

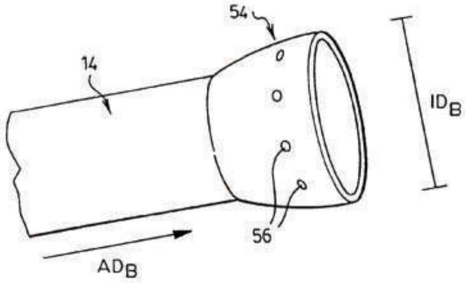

Figure 4.5. The structure of the second pipe to be joined. For numerical symbols see text. [Adapted from Allouche, E., **US Patent 6,918,618**, Jul. 19, 2005.]

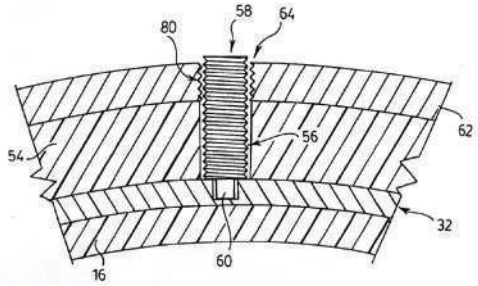

Figure 4.6. Use of radial fasteners to join two pipes. [Adapted from Allouche, E., **US Patent** 6,918,618, Jul. 19, 2005.]

around the outer surface (20) of the spigot end (16), such that the groove (22) has a bottom surface, a length L in the axial direction AD_S, a forward radial edge (26) and a trailing radial edge (28). The forward radial edge (26) is closer to the first axial opening (18) of the first PVC pipe (12) that is the trailing radial edge (28).

The second PVC pipe (14) (Figure 4.5) has an axial direction AD_B and a bell end (54). There is a plurality of angularly-spaced-apart holes (56) extending radially through the bell end (54) of the second PVC pipe (14). The bell end (54) has an inside diameter ID_B greater than the outside diameter $0D_S$ of the spigot end (16) of the first PVC pipe (12) (Figure 4.4).

As illustrated in Figure 4.3, the bell end (54) of the second PVC pipe (14) is fitted onto the spigot end (16) of the first PVC pipe (12) in the same axial direction AD_B as the axial direction AD_S of the first PVC pipe (12).

Figure 4.6 shows that there is provided a set of radial fasteners (58) with each fastener extending through one of the angularly-spaced-apart holes (56) extending radially in the bell end (54) of the second PVC pipe (14) (Figure 4.3).

The radial fasteners are arranged such that a first end portion (60) of each radial fastener (58) abuts or contacts against the relevant radial shoulder of the inner ring (32). Further details can be found in the invention.

PVC assembly for the crankcase ventilation system. [Data from Spix, T. A., **US Patent 6,782,878**, Aug. 31, 2004.]

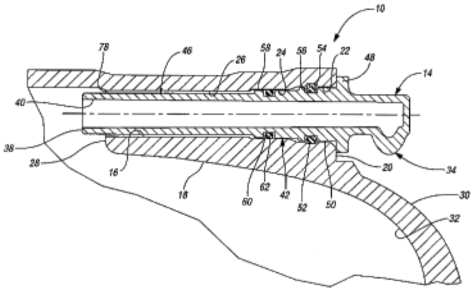

Figure 4.7. PVC assembly for crankcase ventilation system preventing frost formation. [Adapted from Spix, T. A., **US Patent 6,782,878**, Aug. 31, 2004.]

PCV fitting (14) (Figure 4.7) includes a tubular body (34) with an inlet end (34) and an outlet end (38) and defining an internal fluid passage (40) between the inlet and outlet ends. The body (34) is formed of a heat and oil resistant plastic suitable for use in a PCV system.

The body (34) of the PCV fitting (14) includes a mounting portion (42), a connecting portion (44) and an isolating portion (46). The mounting portion includes a flange (48) which, in assembly, engages the mounting face (20) of the manifold (12). A relatively large mounting diameter (50) extends longitudinally from the mounting flange and, in assembly, extends in close fitting relation with the mounting bore (22) of the PCV inlet opening (16) of the manifold. A retaining groove (52) in the mounting diameter carries an O-ring seal and retainer member (54) which is received in an internal groove (56) of the mounting bore (22). The seal (54) expands into the groove with a snap-like motion upon assembly and acts to releasably retain the fitting (14) within the mounting bore (22) of the intake manifold (12). Inwardly adjacent to the mounting diameter (50), fitting (14) includes a reduced diameter sealing portion (58) carrying an external groove (60) in which is carried a primary O-ring seal (62). Seal (62) engages the smooth sealing bore (24) of the manifold to act as a primary seal preventing any transfer of gases between the interior of the manifold and the atmosphere external to the manifold.

When the engine is operated at very cold ambient temperatures, water that has accumulated in the engine oil and crankcase will vaporize and condense in the PCV system passages. The condensate may collect in the PCV passage where the delivery fitting enters the manifold due to loss of heat from the crankcase vapors to the fitting which is cooled by the walls of the manifold exposed to below freezing temperatures of the intake air. If the frost builds up in the passage, it may become blocked, preventing the normal operation of the PCV system in disposing of crankcase vapors through the engine induction system and cylinders. The invention proposes the system which can be economically implemented to deal with the above problems.

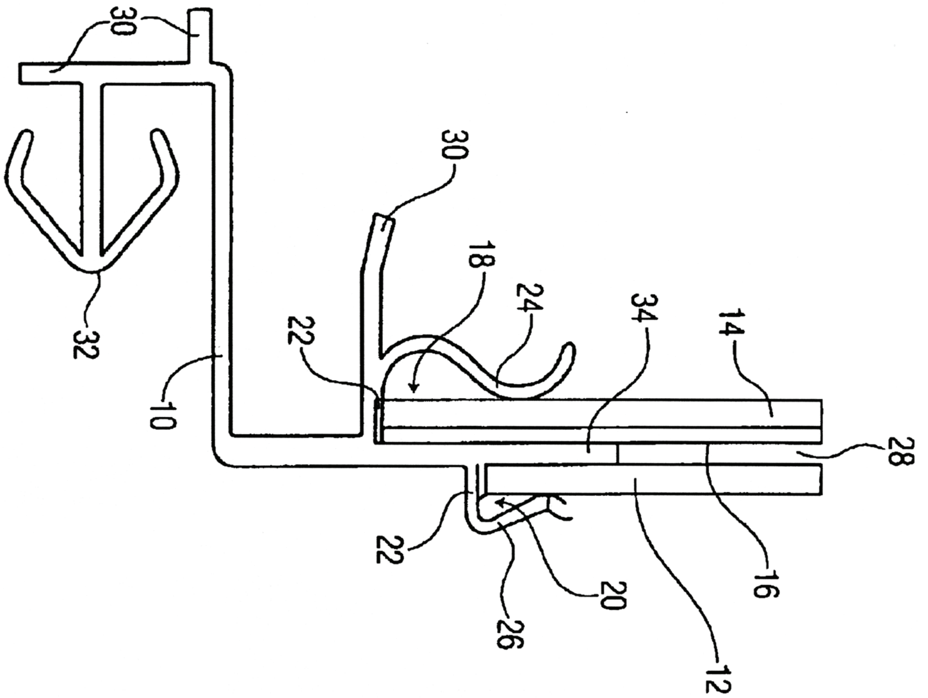

Figure 4.8. Screen protection having several mounting and fitting features. Details in text. [Adapted from Senkler, C. E., **US Patent 6.717,627**, Apr. 6, 2004.]

Integrated screen protection and holder. [Data from Senkler, C. E., **US Patent 6.717,627**, Apr. 6, 2004.]

Figure 4.8 shows a part manufactured from PVC to protect the lens assembly of a projection TV. There are many elements in the design, including a snap-fit connector (32), a standoff (30), protrusions (24) and (26), used for the connection (32), spatial orientation (30), and angular orientation (24), (26).

Optical fiber cable. [Data from Quiroz, D., **US Patent 6,647,188**, Nov. 11, 2003.]

Figure 4.9 shows an optical fiber ribbon assembly (2,3) including a plurality of aligned optical fibers (27) and a laminated structure surrounding the optical fibers. The laminated structure includes a clear polyvinylchloride extrusion layer (22) bonding the fibers together, and a pair of Kapton layers (21) laminated over the PVC extrusion layer. Additional Kevlar members (34) may be aligned with the fibers and embedded in the PVC extrusion layer and the Kapton layers, thereby providing the fibers with extra protection from tensile loads. Figure 4.9 shows two different versions of the invention as discussed above.

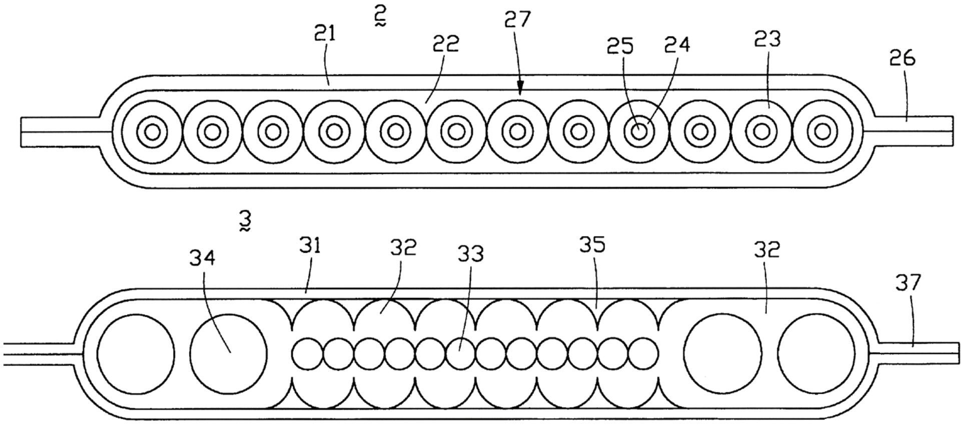

Figure 4.9. Optical ribbon assemblies. [Adapted from Quiroz, D., **US Patent** 6,647,188, Nov. 11, 2003.]

Optical fiber cable. [Data from Bourget, V., **US Patent 6,647,186**, Nov. 11, 2003.]

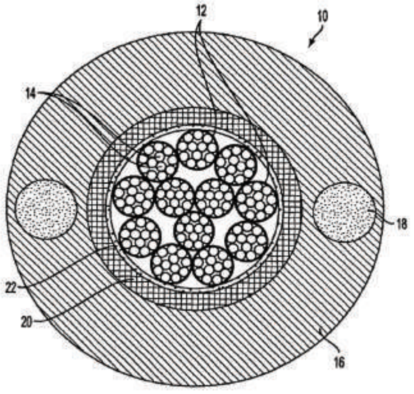

Figure 4.10. Optical cable. [Adapted from Bourget, V., **US Patent 6,647,186**, Nov. 11, 2003.]

Figure 4.10 shows the optical cable (10) which includes an assembly of flexible tubes (12), each of which accommodates a bundle of conventional optical fibers (14). The assembly of tubes (12) is covered with a sheath (16). The tubes (12) preferably extend inside the sheath (16) in a conventional helical or SZ assembly.

Filamentary form members (18) forming tensile reinforcements are provided at the periphery of the assembly of tubes (12). The optical cable (10) includes two diametrally opposed strength members (18) buried in the wall delimiting the sheath (16). The structure and the assembly of the strength members (18) in the sheath (16) are conventional.

The optical cable (10) includes mechanical reinforcing braids (20) made of aramid, for example, extending radially between the tubes (12) and the sheath (16) in an annular assembly, for example in a helix.

The optical cable (10) includes conventional sealing means. The sealing means can consist of a sealing tape (22) extending radially between the tubes (12) and the sheath (16), more particularly between the tubes (12) and the assembly of reinforcing braids (20).

Lightweight greenhouse structure for rapid assembly. [Data from Williams, D. A.; Williams, C. L., **US Patent 6,618,988**, Sep. 16, 2003.]

Figure 4.11 shows several elements of the entire assembly including angled fittings (64,66,68,70,72,74), T fittings (20,30), triple fittings (22,24,32,34), anchoring O-rings (142,144,146), retainer (126), push-in/pull-out retainer (162), and clips (190). All these elements are useful in the fast assembly of this invention and many other products.

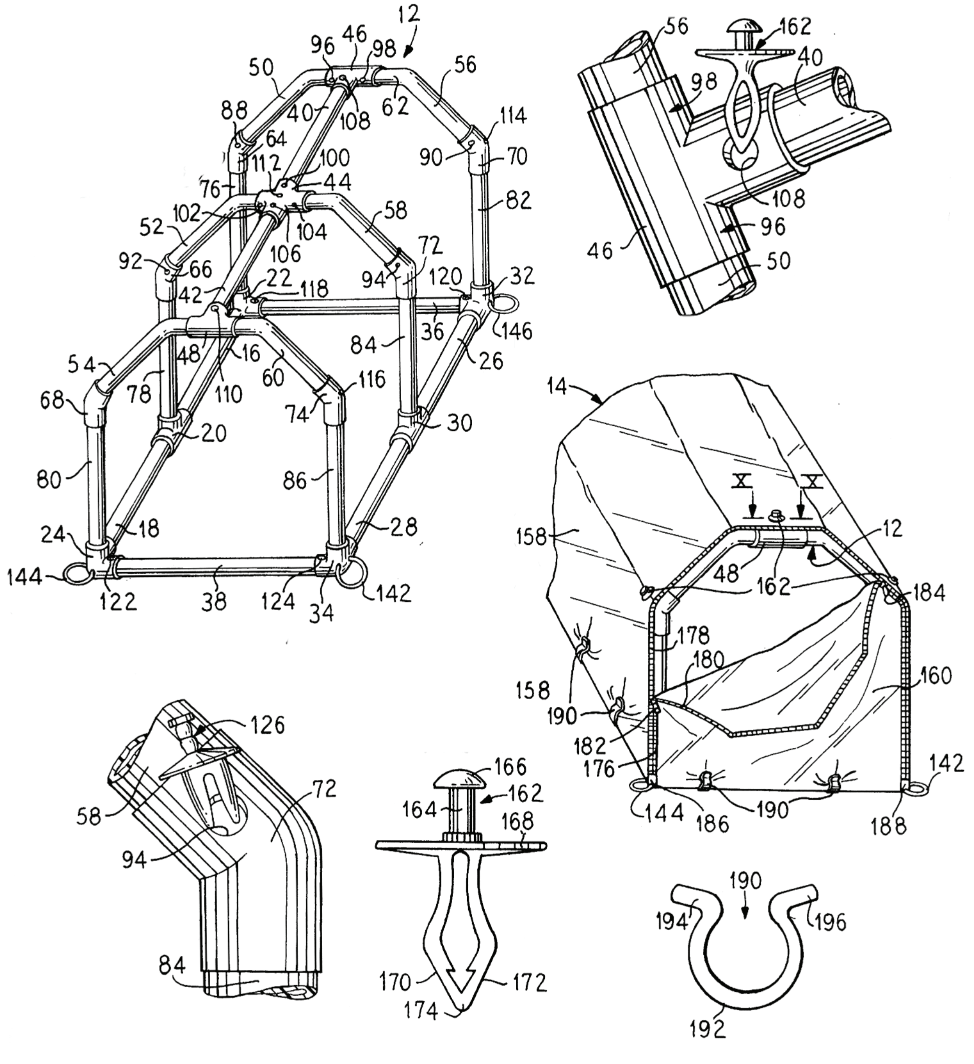

Figure 4.11. Lightweight greenhouse structure designed for rapid assembly. [Adapted from Williams, D. A.; Williams, C. L., **US Patent 6,618,988**, Sep. 16, 2003.]

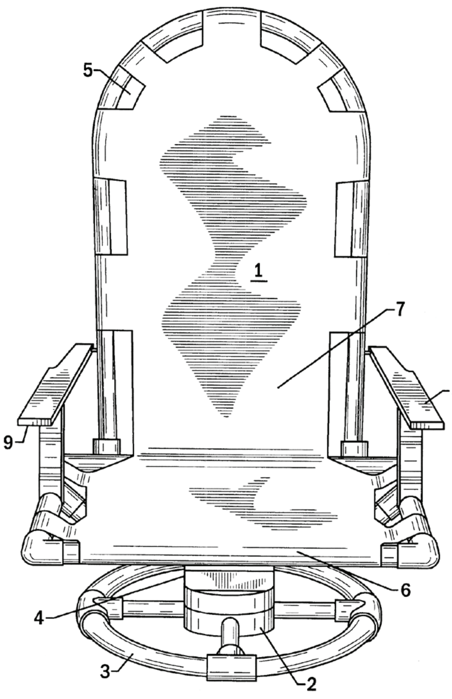

Figure 4.12. Swivelable beach chair. [Adapted from Almerico, R. A., **US Patent 6,575,532**, Jun. 10, 2003.]

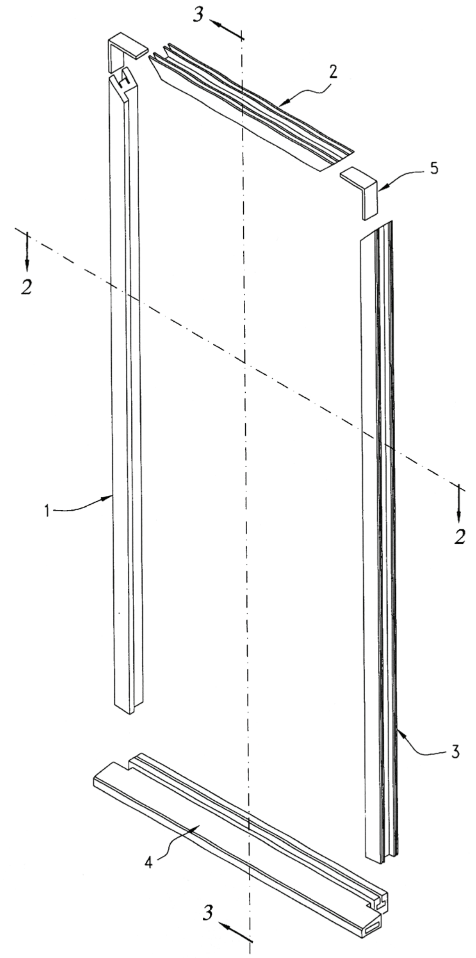

Figure 4.13. Adjustable door frame assembly. [Adapted from Wang, C. K.-U., **US Patent 6,530,183**, Mar. 11, 2003.]

Swivelable beach chair. [Data from Almerico, R. A., **US Patent 6,575,532**, Jun. 10, 2003.]

Figure 4.12 shows a chair (1) designed to be used on the beach. The chair (1) consists of the seat (6), the underpinning (4), the swivelable means (2), and the base (3). It has a back (5), an armrest (8) and an adjustable recline feature (9). The drawing shows the method of assembly. Further details are included in the patent.

Adjustable door frame assembly. [Data from Wang, C. K.-U., **US Patent 6,530,183**, Mar. 11, 2003.]

Figure 4.13 shows an adjustable door frame assembly which includes an h-shaped top or upper frame (2) made of PVC foamed plastic co-extruded with a soft gasket, an h-shaped left frame (1), an h-shaped right frame (3), two L-shaped corner connecting metal pieces (5), reinforced metal pieces (7) having a U-shaped cross-section and a bottom threshold (4). The assembling procedures are also illustrated. First, the left frame (1) and the top frame (2) are attached, preferably by screws with a corner connecting metal piece (5), followed in the same way by fixing the right frame to a second corner connecting metal piece (5) to form a U-shaped frame. Finally, the ends of the left and the right frames (1) and (3) are placed into preset holes at two ends of a bottom threshold (4).

Lightweight PVC door panel for trucks and the method of assembly.

[Data from Dodson, G. C.; Takagi, K., **US Patent 6.513,862**, Feb. 4, 2003.]

Figure 4.14 shows a door assembly (70) according to the invention. The door assembly (70) comprises a plurality of interlocked door panels (20). Each of the door panels (20) defines a female portion (30), a male portion (40) and a panel body portion (50). To minimize the overall weight or mass of the door panel (20) while maintaining sufficient strength, rigidity, and durability, the panel body portion (50) and the male portion (40), the combined size of which significantly exceeds that of the female portion (30), are formed from a material having a significantly lower density than is the female portion (30). For example, the panel body portion (50) and the male portion (40) are formed from PVC, and the female portion (30) is formed from aluminum.

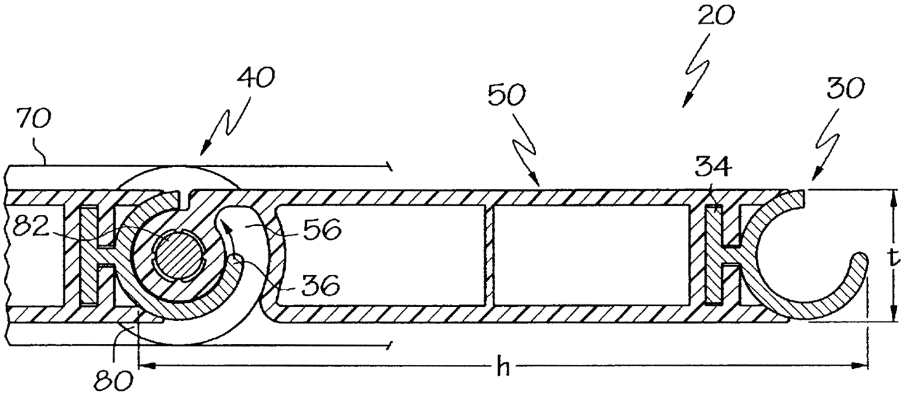

Figure 4.14. Lightweight door pane. [Adapted from Dodson, G. C.; Takagi, K., **US Patent 6.513,862**, Feb. 4, 2003.]

Magnet holder.

[Data from Olson, A. M., **US Patent 6,245,006**, Jun. 12, 2001.]

Magnetic therapy is considered an effective non-invasive, no-side-effects treatment that can speed recovery from a variety of conditions ranging from tendinitis and back pain to migraine headaches and a neuromuscular condition known as fibromyalgia. Application of one or more small, powerful magnets to the area of an injury will relieve pain and accelerate healing. Figure 4.15 is a bottom perspective view of a magnet assembly incorporating a holder in accordance with the present invention, the body sheet of the holder being broken away and shown partially in cross-section for clarity. The holder (10) for a therapeutic magnet assembly comprises four permanent magnets (12,13,14,15), and an annular armature (16) positioned against one side of the array of magnets. The holder (10) comprises two flexible plastic sheets (18) and (19) (made out of PVC), the first (18) constituting the body of the holder and being shaped with indentations forming cavities for receiving the magnetic parts, and the second (19) constituting the cover of the holder for overlying and closing the cavities to retain the magnetic parts in place.

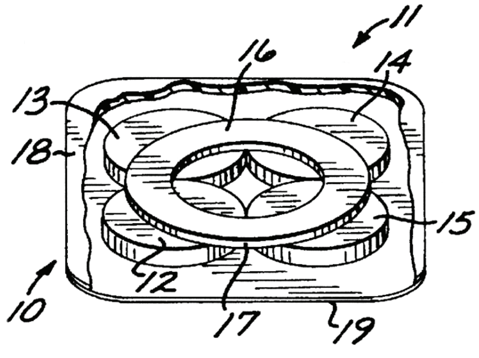

Figure 4.15. Magnet holder. [Adapted from Olson, A. M., **US Patent 6,245,006**, Jun. 12, 2001.]

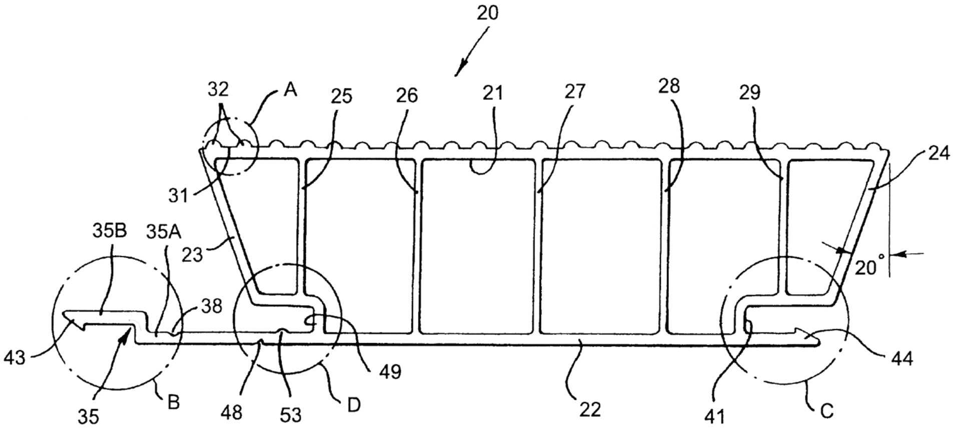

Figure 4.16. Modular construction element. [Adapted Davis, H. H., **US Patent 6,199,340**, Mar.13, 2001.]

Modular construction element. [Data from Davis, H. H., **US Patent 6,199,340**, Mar.13, 2001.]

The invention is applicable to the construction of boat docks, piers, decks, patios, walkways, pontoon boat floors, and the like. Figure 4.16 is an end view of one of the decking plank. The decking plank (20) includes integrally-formed top and bottom walls (21) and (22), and opposing side walls (23) and (24). Integral reinforcing ribs (25,26,27,28,29) are located between the side walls (23) and (24), and bridge the top and bottom walls (21) and (22). The ribs (25-29) extend longitudinally from one end of the decking plank (20) to the opposite end for increasing

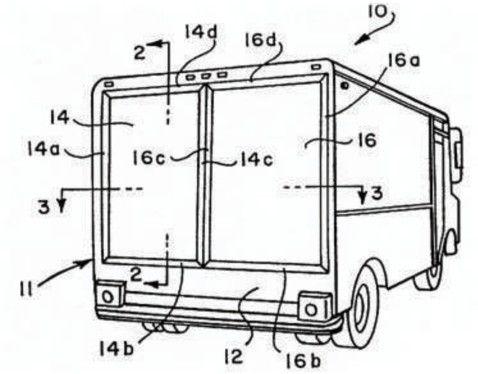

Figure 4.17. Swing door assembly. [Adapted from Kellogg, C. F.; Dietrich, A. T., **US Patent 6,158,171**, Dec. 12, 2000.]

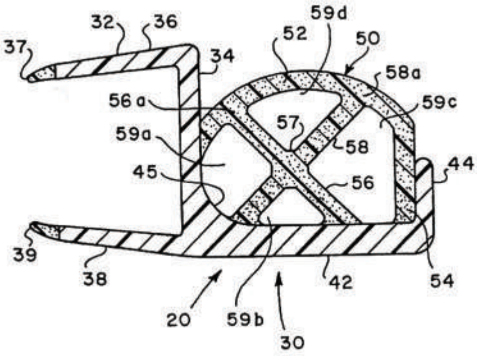

Figure 4.18. Details of the seal. [Adapted from Kellogg, C. F.; Dietrich, A. T., **US Patent 6,158,171**, Dec. 12, 2000.]

its load-resisting capacity. The side walls (23) and (24) converge towards the bottom wall (22) at an angle of about 20 degrees. The connecting portion (35B) and channel (41) include interfering shoulders (43) and (44) providing a snap-attachment to lock the adjacent decking planks (20) to each other while permitting a limited degree of relative lateral movement between them.

Swing door seal assembly. [Data from Kellogg, C. F.; Dietrich, A. T., **US Patent 6,158,171**, Dec. 12, 2000.]

Figure 4.17 shows swing door panels of the invention (14c,16c). Figure 4.18 shows details of seal and retainer assembly. Each section of the seal and retainer assembly (20) includes an elongated section of retainer member (30), which is characterized by a channel-shaped portion (32) having a generally planar web (34) and opposed substantially coextensive flanges (36) and (38). The flanges (36) and (38) are spaced apart in an unrestrained position converging slightly toward each other, as fabricated. The resilient tips (37) and (39) curve inwardly toward each other so that they engage the opposed inner and outer parallel surfaces of the panels (14) and (16) to form a substantially weather-tight seal between the panel edges and the channel portion (32). The retainer member (30) also includes a seal support base part (42).

Connectors of PVC gate. [Data from Brown, R. W., **US Patent 6,131,888**, Oct. 17, 2000.]

Figure 4.19 shows all the structural elements of a PVC gate. It includes four elbow connectors (10) and picket holes (32) used for connecting the gate elements.

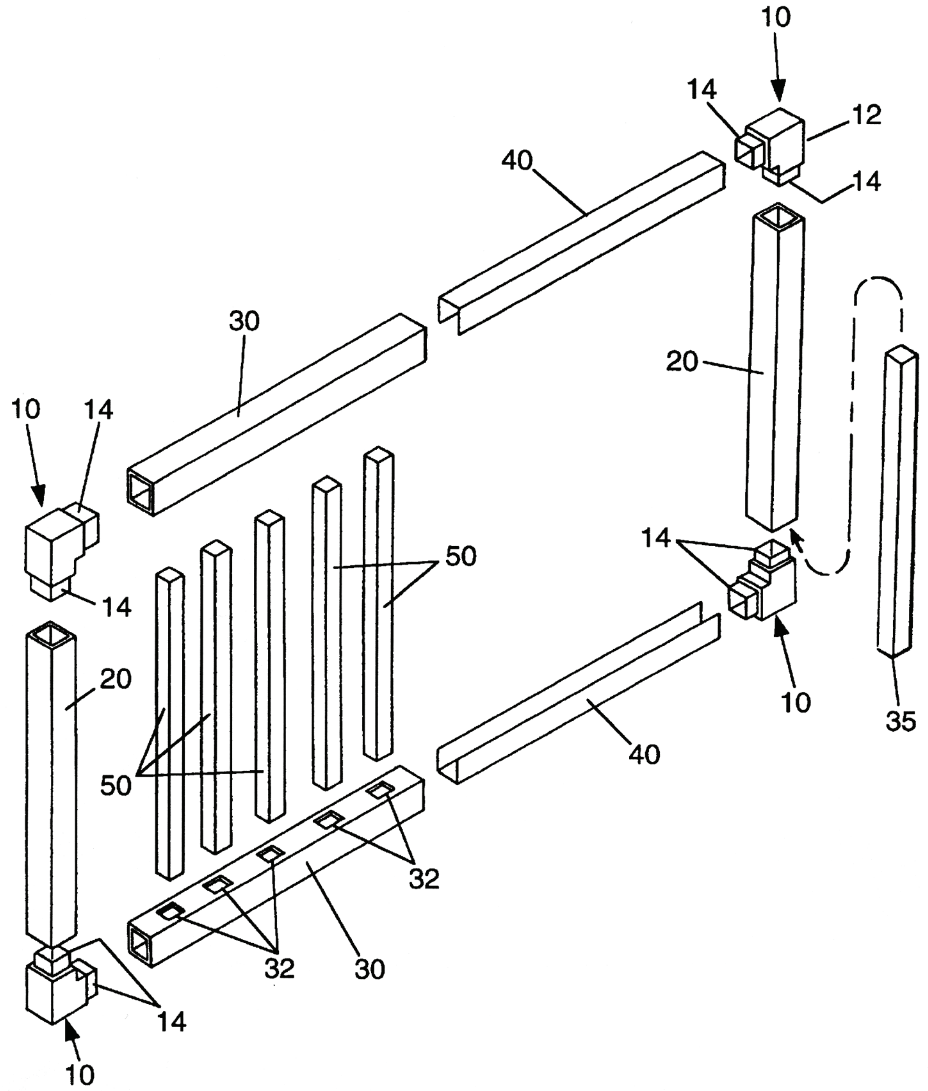

Figure 4.19. Connectors of the PVC gate. [Adapted Brown, R. W., **US Patent 6,131,888**, Oct. 17, 2000.]

Light building assembly system. [Data from Doran, R. G., **US Patent 6,088,970**, Jul. 18, 2000.]

Figure 4.20 is a cross-sectional view of the roof section and the wall section, showing in detail the locking mechanisms. The PVC track (20) is secured to a base (floor) (22). A wing (32) is added to the outside face of the top track by inserting the top and bottom tongue of the wing into the top and bottom groove of the track. Therefore, the top and bottom tracks are one and the same except that

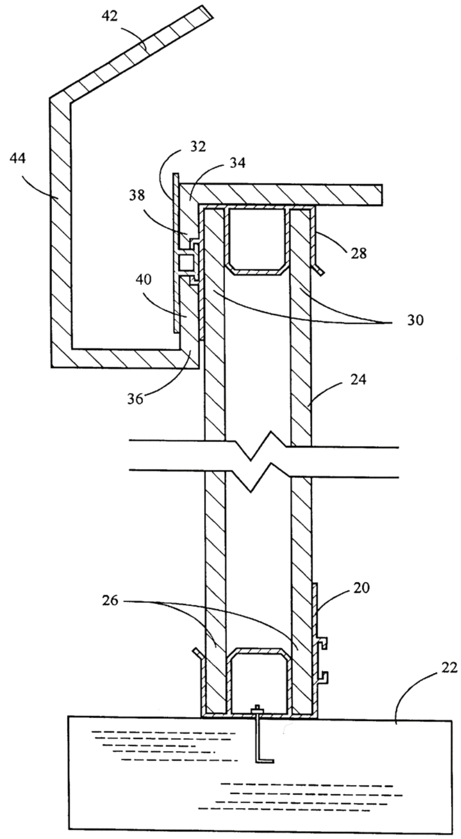

Figure 4.20. Light building assembly system. [Adapted from Doran, R. G., **US Patent 6,088,970**, Jul. 18, 2000.]

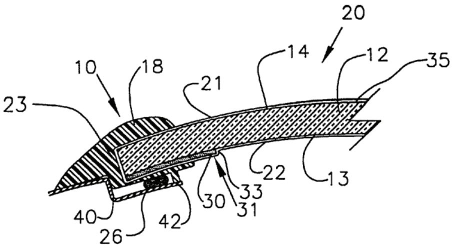

Figure 4.21. Glazing module. [Adapted from Kobrehel, M. D.; Vanarak, V. C., **US Patent 5,915,780**, Jun. 29, 1999.]

the top track has an added wing, which creates two grooves on the outer side of the wall. After the wing has been inserted, the space created (34) and (36) is used to house the ceiling lip (38) and the roof lip (40). Each roof section (42) is placed into position on top of the 45/8" wide top track and secured by use of adhesive. The ceiling lip (38) is turned 90 degrees down vertically and inserted into the groove (34) and secured with adhesive. The roof panel (44) is turned vertically down 75 degrees or thereabout to create a fascia panel, then turned 90 degrees horizontally back toward the building to build a sofit, then vertically 90 degrees. The vertical roof lip (40) locks into a groove (36) and is secured by use of adhesive.

Plastic glazing module. [Data from Kobrehel, M. D.; Vanarak, V. C., **US Patent 5,915,780**, Jun. 29, 1999.]

Figure 4.21 gives a cross-sectional view of an encapsulated plastic glazing window module. The module has a glazing assembly (20) having an exterior surface (21), and interior surface (22) and a perimeter surface (23); an encapsulation material (18) encapsulating the glazing assembly; and an adhesive (26) for securing the glazing assembly to the motor vehicle wall (40). The glazing assembly (20) comprises a transparent plastic substrate (12) having an interior (13) and exterior sides (14), which is injection molded onto a frit film (30).

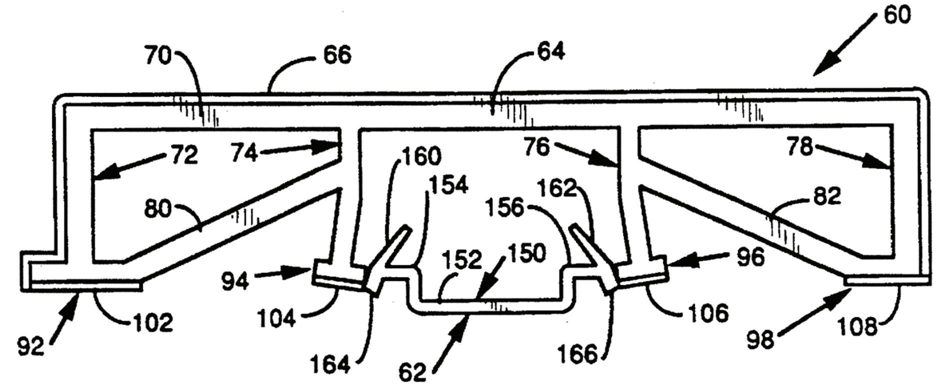

Figure 4.22. Snap connection. [Adapted Anres, T., **US Patent 5,642,592**, Jul. 1, 1997.]

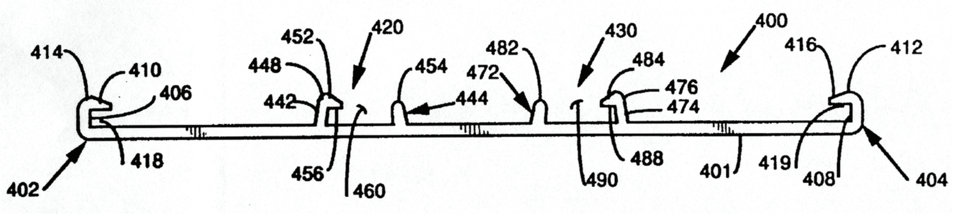

Figure 4.23. Snap connector. [Adapted Anres, T., **US Patent 5,642,592**, Jul. 1, 1997.]

Floor assemblies. [Data from Anres, T., **US Patent 5,642,592**, Jul. 1, 1997.]

Figure 4.22 shows one version of connectors in which to connect the extrusion (60) to the snap connector (62), the extrusion (60) is merely pressed down on the snap connector (62), thus forcing the resilient legs (74) and (76) to bend outwardly. The bending of the legs (74) and (76) is facilitated by the angular orientation of flanges (160) and (162), which act as a pilot surface to bend the legs (74) and (76) outwardly. Once the legs (74) and (76) are pressed down far enough to clear the bottom sections (164) and (166) of the flanges (160) and (162), the legs (74) and (76), along with foot sections (94) and (96), snap into position. The extrusion (60) is thus securely connected to the snap connector (62).

Figure 4.23 shows a snap connector (400) which can be mounted on the wide vertical side of a wood joist to facilitate securement of the vertically oriented plastic extrusions. The snap connector (400), which is made of an extruded polyvinyl chloride material, includes an elongated base (401) having a pair of opposed elongated end flanges (402) and (404). Each flange (402,404) includes a first section (406,408) which extends perpendicularly to the base (402) and a second section (410,412) which in turn extends perpendicularly from the first section (406,408). Each second section (410,412) includes a pilot surface (414,416). The flanges (402,404) each define a recessed space (418,419). The snap connector also

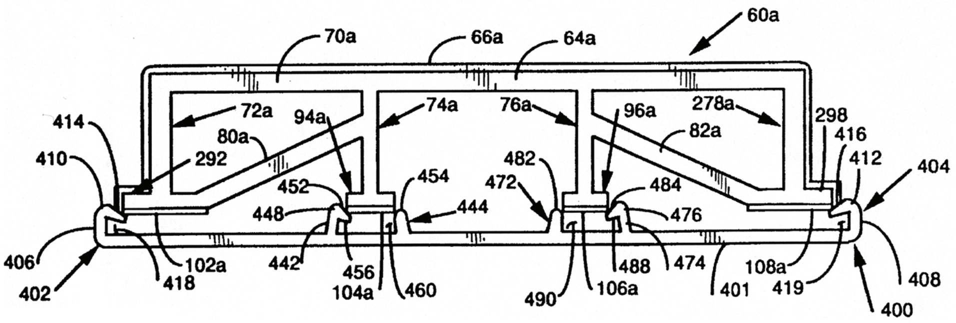

Figure 4.24. Snap connector aligned with plastic extrusion for snap fit connection. [Adapted Anres, T., **US Patent 5,642,592**, Jul. 1, 1997.]

includes two locking members (420) and (430). Locking member (420) consists of a pair of flanges (442,444) which extend at a slight inward angle from a line perpendicular to the base (402). Flange (442) includes an inwardly facing lip (448). Lip (448) has an upper pilot surface (452) and a lower surface (456) which is parallel to the base (402). Flange (444), on the other hand, does not include a lip but does have an upper pilot surface (454). The flanges (442,444) define a locking space (460).

Figure 4.24 shows how a plastic extrusion, in this case plastic extrusion (60a), engages in to a snap connector (400). The extrusion (60a) is merely pressed down on the snap connector (400). The legs (292,94a,96a,298) engage against the respective pilot surface, i.e., pilot surface (414) for foot section (292); pilot surfaces (452,454) for foot section (94a); pilot surfaces (482,484) for foot section (96a); and pilot surface (416) for foot section (298). Once the legs (292,94a,96a,298) are pressed down far enough to clear flanges (402,442,444,472,474,404) respectively, the legs (292,94a,96a,298) snap into recessed spaces (418,460,490,419), respectively. The extrusion (60a) is thus securely connected to the snap connector (400).

PVC pipe cement. [Data from Waldrop, M. W.; Walsh, W. C., **US Patent 5,852,091**, Dec. 22, 1998.]

Raw material	A	B
	Concentration, wt%	
Methyl ethyl ketone	56	56
N-methyl pyrrolidone	16	16
Tetrahydrofuran	4	4
Cyclohexanone	4	4

PVC pipe cement. [Data from Waldrop, M. W.; Walsh, W. C., **US Patent 5,852,091**, Dec. 22, 1998.]

Raw material	A	B
	Concentration, wt%	
Neopentyl glycol	10	
1,6-Hexanediol		10
PVC (Geon 191)	10	
PVC (Geon 110X334)		10

Low VOC pipe adhesive. [Data from Patel, N. D., Brown, M. W., **US Patent 5,422,388**, Jun. 6, 1995.]

Raw material	Concentration, parts
PVC (inherent viscosity 0.68)	13.5
Acrylic VS-100	16.5
THF	50
Cyclohexanone	20
Viscosity, cP	1880
Lapshear strength (72 h), psi	1322
VOC, g/l	401

PVC pipe adhesive. [Data from Bierens, J P M, Klerks, J P M, **World Patent WO2013122458**, Aug. 22, 2013, *Bison International BV.*]

Raw material	Concentration, parts
CPVC	8
PVC/Ac copolymer	8
1,3-dioxolane	30
Methyl ethyl ketone	36.5
Cyclohexanone	15
Thickener	2
Tin stabilizer	<0.5
Diverse additives	<0.5

Pressure sensitive adhesive for PVC films. [Data from Cimpeanu, C-E, Beyers, C P, Dragon, A, **US Patent US2012/0244350**, Sep. 27, 2012, *BASF SE*.]

Raw material	Concentration, wt%
2-Hydroxybutyl acrylate	67.49
Methyl methacrylate	12
Methyl acrylate	7.9
Acrylonitrile	5
2-Hydroxypropyl acrylate	2.16
2-Ethylhexyl acrylate	1.9
Acrylic acid	1.5
Allyl methacrylate	0.05

Adhesive. [Data from Herold, J.; Geisen, I., **US Patent 4,525,234**, Jun. 25, 1985.]

Raw material	Concentration, parts
PVC (K=74)	7.5
VC/VAc copolymer (90/10)	7.5
Dimethylcyclohexyl phthalate	44
Barium sulfate	40
Condensation product of dimerized fatty acids and polyamines (amine number=250)	1
Tensile shear strength, N/cm^2	170

Further reading:

Handbook of Plastic Joining. **A Practical Guide**. *William Andrew Publishing*, Norwich, 1997.

4.12 LAMINATION

Several methods of lamination are used, such as the already described use of calender, coating of web substrates which is discussed in Section 23, but also some less conventional methods which are given as examples below.

4.12.1 PATENTED INVENTIONS

Flexible laminated pipe. [Data from Backman, A. L.; Dalai, G. T.; Vontorcik, J. J., **US Patent 7,223,456**, May 29, 2007.]

Raw material	Concentration, parts
CPVC (TempRite 674x571)	100
PVC (BCP-65)	10
Dibutyltin bis-(2-ethylhexylmercaptoacetate)	2.4
Chlorinated polyethylene (Tyrin 3611P)	2
Chlorinated polyethylene (Tyrin 4211P)	1.5
Oxidized polyethylene	1
Fischer Tripsch wax	0.5
Paraloid KM-330	4
Titanium dioxide	5

A three-layer pipe is obtained by coextrusion. The inner (or core layer) is made from CPVC/PVC blend; the outer layer is copolyester elastomer (which is not moisture resistant and thus requires protection by an outer sheath which is made from thermoplastic polyurethane.

PVC skin skateboard. [Information from Thompson, D R, **US Patent US20120018970**, Jan. 26, 2012.]

Skateboards are decorated. The best mode of production of skin skateboard is to print on the outside surface of a foil sheet which is then laminated to the PVC. It is also possible to use a bilayer printed film construction by having print on the inside surface of a transparent sheet which then receives a foil sheet underneath the transparent sheet. The bi-layer printed film construction can be first printed in a roll and laminated together in a roll of printed film, for later lamination to a PVC sheet. Another manner of printing would be to print on the inside surface of the PVC sheet and laminate a foil underneath the PVC sheet.

Vehicle seat. [Data from Ashida, N.; Mayajima, I.; Sugimoto, A., **US Patent 6,832,421**, Dec. 21, 2004.]

Figure 4.25 shows that the seat includes a cushioning material (20) disposed on a bottom plate (30). The cushioning material (20) is covered with a skin material (10). The skin material (10) and the cushioning material (20) are bonded with an adhesive (40) which is coated on both sides (cushioning material and skin).

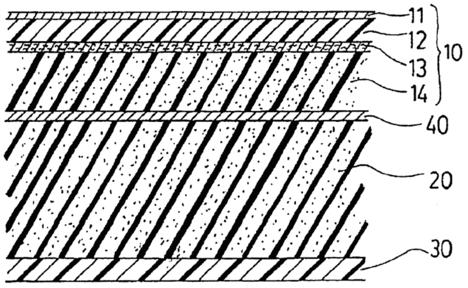

Figure 4.25. Vehicle seat. [Adapted from Ashida, N.; Mayajima, I.; Sugimoto, A., **US Patent 6,832,421**, Dec. 21, 2004.]

The skin material (10) is a laminate of a PVC layer (12) at the surface, a substrate fabric (13) and a closed-cell cellular synthetic resin (14). The PVC layer (12) and the closed-cell cellular material (14) are laminated with the substrate fabric (13). The closed-cell cellular material (14) is present between the PVC layer (12) and the substrate fabric (13), and the cushioning material (20). The closed-cell cellular material (14) is a crosslinked cellular material, more specifically, a PVC cellular material. The cushioning material (20) is made out of polyurethane foam.

Radio frequency identification card. [Data from Vogt, W, Looser, A, Looser, C, Braun, C, **World Patent WO2013032921**, Mar. 7, 2013, *Indentive Group, Inc.*]

Smartcard technology is directed to structures with embedded integrated circuit units. Smart cards can be contact-based or contactless. The RFID technology is directed to wireless communication between one object, typically referred to as a RFID tag, and another object typically referred to as an RFID reader/writer. RFID technology, and smartcard technology in general has been adopted and is increasingly being used, in virtually every industry, including, for example, manufacturing, transportation, retail, and waste management. The card structure includes antenna assembly and integrated circuit unit coupled with contact pads. The card layers can be constructed from PVC because it melts before burning. Also, additives can be included to change the characteristics of the card layers when heated. In this way, it is possible to create a material stack to melt within a range of temperatures and make the lamination of the card more controllable by having layers in the stack soften at different temperatures.

Multilayer PVC/fluorinated polymer structure for protecting the rear of solar panels. [Data from Bonnet, A, Devisme, S, Ramfel, B, Bizet, S, **US Patent US20140044976**, Feb. 13, 2014, *Arkema France.*]

Raw material	Concentration, wt%
Lacovyl GB 1040	71.1
Micromya ($CaCO_3$)	7.9
Kane ACE B 382 (impact modifier)	2.1
Plastistrength 770 (processing aid)	0.7

Multilayer PVC/fluorinated polymer structure for protecting the rear of solar panels. [Data from Bonnet, A, Devisme, S, Ramfel, B, Bizet, S, **US Patent US20140044976**, Feb. 13, 2014, *Arkema France*.]

Raw material	Concentration, wt%
Internal lubricant	1.1
External lubricant	0.3
Ca/Zn heat stabilizer	3.9
Kronos 2220	2.6
Glass fiber	10.3

Exterior automotive laminate. [Data from Johnson, J. R.; Truog, K. L.; Enlow, H. H.; Buehne, W. J.; Young, F., **US Patent 6,042,678**, Mar. 28, 2000.]

Raw material	Concentration, parts
PVC (Geon 199)	48.82
Aromatic solvent (Hi-Sol 10)	19.39
2-ethylhexyl acetate	6.46
UV absorber (UV 531)	1.96
Ba/Zn thermal stabilizer (MX 2181)	2.93
Epoxy thermal costabilizer	1.93
Acrylic copolymer (B 99)	2.44
Plasticizer (G-59)	3.91
Black dispersion	12.14

The laminate sheet is a flexible decorative sheet for use in surfacing an automobile body panel. The laminate revealed in this invention contains several layers, including clearcoat, tie coat, color coat, and adhesive layer. Clearcoat is formulated from polyvinylidene fluoride (to assure excellent weather resistance), tie coat is formulated from acrylic (good adhesion to both clearcoat and colorcoat and weather resistance), colorcoat was formulated from PVC (see formulation in the above table) and adhesive was pressure sensitive acrylic formulation.

Plastic laminate. [Data from Kitazawa, K.; Nakamura, E., **US Patent 5,350,550**, Sep. 27, 1994.]

Raw material	Top layer	Foamed layer
	Concentration, parts	
PVC	100	100
DOP	50	60
Ba/Zn stabilizer	3	
Calcium carbonate		80
Titanium dioxide		15
Azodicarbonamide		5
Na/Zn liquid stabilizer		3
Mineral spirit		10

Decorative laminate. [Data from Kauffman, W. J.; Colyer, T. D.; Dees, M., **US Patent 4,599,264**, Jul. 8, 1986.]

Raw material	Base layer	Top layer
	Concentration, parts	
PVC (Tenneco 1732)	100	
PVC (Occidental 605)		100
DOP	35	
Santicizer S-711		34.8
Secondary plasticizer (2,2,4-trimethyl-1,3-pentanediol diisobutyrate)	17	5
Epoxidized soybean oil	3	2
Tin stabilizer (Mark 275)	1	
Zinc octoate (ABC-18)		1
Azodicarbonamide (Kempore Af)		1.6
Pigment		0.5-2

The base layer was coated on the substrate; the top layer was printed using a rotary screen roller before the material was heat-treated.

4.13 METALIZATION

Metalization of PVC is not in common use, but there are useful examples in the patent literature given below. It is possible that PVC is less used for metalization because the HCl evolved affects the quality of the metalized layer (adhesion and reflective functions). Adhesion also suffers from the low affinity of PVC and metal surfaces and plasticizer bleeding to the surface.

4.13.1 PATENTED INVENTION

Article with metalized surface. [Data from Ueno, S, Nomura, H., **US Patent 4,603,057**, Jul. 29, 1986.]

Raw material	Concentration, parts
PVC	100
DOP	60
Thermal stabilizer	not specified

This invention avoids problems of adhesion by precoating the PVC surface with organosilicone substance prior to metalization. PVC of the above formulation was formed into a sheet which was then subjected to metalization. The sheet was placed in a plasma chamber of a plasma generating apparatus which was evacuated to a vacuum of 10^{-3} Torr, controlled, and maintained at a pressure of 0.1 Torr by the balance of a continuous introduction of air and evacuation. At this state, the vapor of trimethylchlorosilane was introduced into the plasma chamber at a constant rate to be admixed with the air flowing through the chamber so that the partial pressures of the air and the silane vapor in the chamber were 0.1 Torr and 0.3 Torr, respectively. While the atmospheric conditions in the plasma chamber were kept as described above, a high frequency electric power of 1 kilowatt at a frequency of 13.56 MHz was supplied to the electrodes for 300 seconds so that low-temperature plasma was generated inside the plasma chamber, and the surface of the resin sheet became covered with a layer of the plasma-polymerized organosilane compound. The thickness of this plasma-polymerized layer was about 100 nm. The plasma-treated resin sheet was placed in an apparatus for vacuum vapor deposition and metalized with aluminum vaporized in a vacuum of $1x10^{-4}$ Torr by induction heating of 10 kilowatts power. The thickness of the formed metalizing layer of aluminum was about 200 nm. The metalized layer was subjected to a normal peel test and no metal was peeled from the surface.

4.14 PHARMACEUTICAL PRODUCTS

4.14.1 FORMULATIONS FOUND IN THE OPEN LITERATURE

Polymeric films for transdermal delivery. [Data from Chantasart, D.; Tocanitchart, P.; Wongrakpanich, A.; Teeranachaideekul, V.; Junyaprasert, V. B., *Pharm. Dev. Technol.*, **23**, 8, 771-9, 2018.]

The patches were composed of film formers (Eudragit) as a matrix backbone, with PVC as a backing membrane and PEG200 used as a plasticizer. To create the transdermal patch, the dried drug-loaded film was removed from the mold, fixed onto an adhesive-coated polyvinylchloride backing membrane and covered with a silicone-coated polyester membrane. The prepared patches showed sustained release of piroxicam over time, and the release kinetics followed the Higuchi model.

4.14.2 PATENTED INVENTIONS

Biodegradable PVC film for pharmaceutical blister packaging [Data from Klaus, W. M.; Marco, P.; Nair, A. S.; Naik, P., **EP2766275A4**, *Bilcare Ltd*, Aug. 5, 2015.]

Raw material	Concentration, kg
PVC homopolymer suspension resin	187
Vinyl chloride/Vinyl Acetate copolymer	243
Methylmethacrylate-butadiene-styrene acrylic copolymer	34.1
Stabilizer	6.33
Dicarboxylic acid ester	21.9
Fatty acid ester of polyfunctional alcohols	1.46
Butadiene/methylmethacrylate/styrene processing aid	1.22
Montanic ester wax	0.487
Mg-silicate based talc	0.414
Bio pro-degradant (Eco-pure™)	3.41

Blister packaging is a popular packaging method for pharmaceutical solid dosage forms, rapidly growing. PVC based films are commonly used for this purpose as they possess suitable properties for thermal formation and protection. The film is stable in aerobic conditions and is bio-degradable under anaerobic conditions. The film was produced by calendering, and blister packaging by thermoforming.

Blister pack for pharmaceuticals [Data from Depla, A., **EP2801475A1**, *Agfa-Gevaert NV, Agfa Health Care NV*, Nov. 12, 2014.]

A preferred structure of an aluminum-based laminate film is OPA/adhesive/aluminum/adhesive/PVC (OPA is biaxially oriented polyamide). PVC is used for two reasons. First, it is commonly used as the contact layer and seal-to layer on pharmaceutical blisters. The second reason is that PVC is very stiff, and does not tend to shrink or spring back during cold forming. Once the cold-forming process is complete, the PVC helps the cavity to hold its shape.

4.15 POWDER COATING

PVC is infrequently used in powder coating but a few useful examples of the process can be found in the patent literature, and these are given below.

4.15.1 PATENTED INVENTIONS

PVC-acrylate powder. [Data from Tresino, J, Cassata, B, **EP2864414A4**, Jan. 6, 2016, *PolyOne Corporation.*]

Raw material	Concentration, wt%
Geon 140x466 (PVC)	62.5
Plas-Check 775 (epoxidized soybean oil)	1.88
SR350K (trimethylolpropane trimethacrylate, curing agent)	25
OMG octyl tin FDA (2807) (heat stabilizer)	1.25
TI-Pure R 960-07 (rutile titanium dioxide)	3.13
Vinnolit P70 (microsuspension PVC)	3.13
RA928 (difunctional bisphenol A/epichlorohydrin-based epoxy)	3.13

Powder coating compositions. [Data from Harmuth, C. M., **US Patent 4,113,681**, Sep. 12, 1978.]

Raw material	A	B
	Concentration, parts	
Polyvinyl chloride terpolymer (VC/VAc/maleic anhydride=80/20/1)	80	90
Methyl methacrylate/butyl methacrylate/methacrylic acid copolymer (69/30/1)	20	10
Plasticizer (triisodecyl trimellitate)	25	22
Liquid epoxy resin (epoxyhydroxypolyether resin of epichlorohydrin and bisphenol A)	4	4.5
Butyltin mercaptide	2.4	2.7
Low molecular polyethylene wax	0.5	
UV absorber (2,4-di-t-butyl phenyl 3,5-di-t-butyl-4-hydroxy benzoate)	0.4	0.45
Carbon black		3
Barium sulfate		8

A blend of the above ingredients was charged onto a two-roll mill having one roll at about 85-95°C and the other roll at room temperature and milled for 20 minutes. The resulting composition was ground into a powder in a pin disc mill cooled to about -72°C with dry ice. The powder was passed through a 140 mesh sieve to remove large particles.

The powder then was sprayed onto phosphatized 24 gauge cold roll steel panels using a Model 222 Ransburg electrostatic powder gun. The gun uses 60 volts of electricity to charge the powder and 60 pounds per square inch air pressure. The coated panels were baked for 5 minutes at 205°C. The resulting finish on each of the panels was about 2-3 mils thick, had excellent adhesion to the substrate, was free from popping and cratering, and had a good appearance. The finish had excellent impact resistance, as shown by an impact test in which the finish was subjected to an impact of 80 and 160 pounds per square inch.

The finish had excellent resistance to corrosion as shown by the salt spray test in which no blisters resulted after 250 hours of exposure to a salt spray and no flaking or peeling of the finish from a scribe mark which was through the finish to the metal. The flaking and peeling of the finish are known as “creep.” After 1000 hours exposure to salt spray, 5/16 of an inch of creep from the scribe mark was noted for formulation A. This was further improved in formulation B. After 500 hours of exposures, no creep or blistering of the finish on the panels was noted. After 1000 hours some small blisters were noted in the finish but no creep. The coated panel was subjected to a mandrel bend test in which a panel was bent at a 90° angle over a mandrel at -7°C. No cracking or chipping on the panel was noted, which indicated that the finish was flexible.

Pulverization of multicomponent polymer waste. [Data from Khait, E.; Riddick, E. G., **US Patent 6,494,390**, Dec. 17, 2002.]

Municipal waste contains a mixture of polymers which could be economically processed in such mixtures if not for low compatibility of mixture polymers when processed in a melted state. This invention suggests a unique way of approaching the problem. Figure 4.26 shows a schematic sectional view of a twin-screw pulverizer (upper drawing) and an elevational view of a representative screw used in practicing the invention when multi-component plastic scrap material is subjected to solid state shear pulverization in the pulverizer barrel (lower drawing). The pulverizer (10) includes a feeder (12) for receiving the polymeric flake scrap feedstock (M) for transport by the twin-screws (14) (only one shown) through the pulverizer barrel zones (Si-SN TOTAL) where (SN TOTAL) corresponds to the total number of pulverizer zones. The first zone (S1) is a material feed zone communicating directly with the feeder (12). Pulverizer barrel zones S2-SN each may be heated by external electric heater bands (BH) on the pulverizer barrel (16), depending on the composition and degree of crystallization of the scrap components being fed to the pulverizer. Zones (S2-SN) are followed by zones (SN+1) to (SN TOTAL) that are cooled by coolant manifold bands or collars (BC) on the pulverizer barrel (16). The solid state pulverization does not

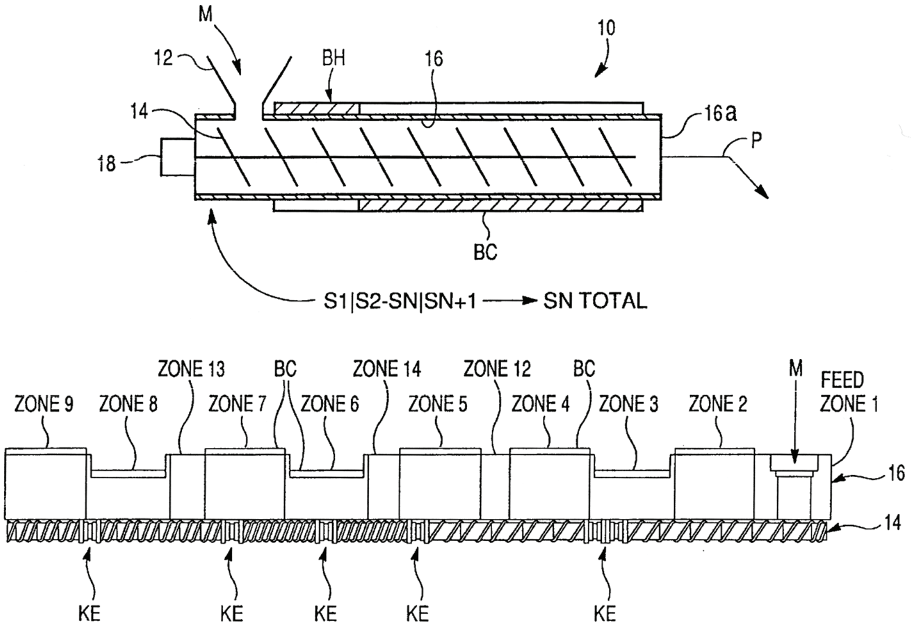

Figure. 4.26. Twin-screw pulverizer (upper drawing) and screw (lower drawing). Details can be found in the text below. [Adapted from Khait, E.; Riddick, E. G., **US Patent 6,494,390**, Dec. 17, 2002.]

involve melting of the polymeric scrap material in the feedstock but may involve softening of one or more of the polymers in the feedstock. Uniform pulverized polymeric particulates (P) (e.g., powder) are discharged at the open (dieless) discharge end (16a) of the pulverizer barrel (16).

Several experiments were performed using different compositions of polymers to simulate some real waste compositions. The ranges of compositions and some results obtained are given in the table below.

Composition	Tensile strength, MPa	Notched Izod, J/m	Flexural strength, MPa	Melt flow index, g/10 min
LDPE/PP/PS/PVC = 50/19/18/13	21.6	27	30.4	1.9
HDPE/LDPE/PP/PET/PS/PVC = 22/34/14/10/12/8	18.9	21	27.4	2.6
HDPE/LDPE/PP/PS/PVC = 15/68/12/2/2	18.7	230	17.1	1.1

The above data show that relatively good results can be obtained by this method as compared with melt processing of waste.

4.16 PRINTING

Printing of PVC surfaces is an important finishing operation which influences decorative values of PVC products. These processes are discussed below based on patent literature. PVC is also used as a protective layer which safeguards the printed surface of PVC and other materials. PVC is also involved in the printing process technology, and equipment and all these topics are discussed below.

4.16.1 PATENTED INVENTIONS

Durable plastic mini card. [Data from Anders, D.; Wright, T., **US Patent 7,384,000**, Jun. 10, 2008.]

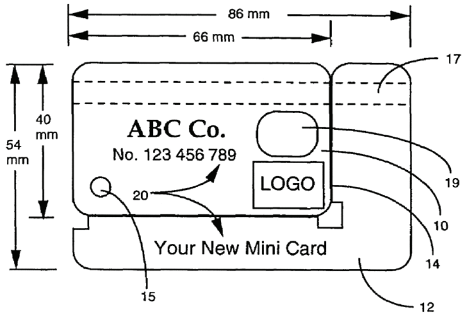

Figure 4.27. Minicard. [Adapted from Anders, D.; Wright, T., **US Patent 7,384,000**, Jun. 10, 2008.]

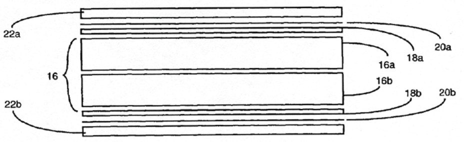

Figure 4.28. Cross-section of mini card. [Adapted from Anders, D.; Wright, T., **US Patent 7,384,000**, Jun. 10, 2008.]

A transparent layer of PVC protects the printed surface of a card against wear. Figure 4.27 shows a view of a mini card and Figure 4.28 shows its cross-section. Figure 4.27 is a top plan view of a mini card (10) connected to disposable support, or frame (12). The mini card and the frame together conform to the size of a standard card, having a generally rectangular shape with a nominal width of 86 mm and a nominal height of 54 mm. The mini card (10) is defined by a recess (14) that is cut into one or both of the surfaces of the standard card. These recesses define the profile of the mini card, which in the illustrated example is also of rectangular shape. The mini card might have a nominal width of 66 mm and a nominal height of 40 mm. An attachment hole (15) is located near one corner of the mini card. The hole (15) can have a diameter of about 5 mm, to accommodate a key ring. If the card is of the type in which data is stored on a magnetic stripe, such a stripe (17) can be provided on the card in a known manner, typically on its back surface, such that it extends across the area of the mini card. If the card is of the smart card type, an electronic module (not shown) containing a memory is embedded in the card. Communication between the module and a terminal can be carried out by means of contacts in an area (19). Alternatively, or in addition, an antenna (not shown) can be incorporated into the structure of the card to provide contactless communication with the electronic module. In the absence of contacts, the area (19) can be used for a security hologram.

Figure 4.28 shows that the card comprises a symmetrical, sandwich-like structure. At the center of the card is a core sheet (16) made from a relatively rigid plastic material, such as polyvinyl chloride. In practice, the core can be constructed of two PVC layers (16a,16b). Each layer can have a thickness of about 0.011 in. Layers of durable plastic material (18a,18b) are disposed on either side of the core (16). These layers might have a thickness in the range of 0.0005-0.0010 in. The durable layers also form printable surfaces upon which the graphics (20) can be printed. The printing is represented by layers of ink (20a,20b) in Figure 4.28. The printed graphics are protected by means of transparent overlay layers (22a,22b) made out of PVC. The overlay layers can have a thickness in the range of 0.001-0.004 in.

3D printing compound [Data from Harrison, G.; Planner, D.; Klamann, J-D; Dennins, H.; Dennins, S., **WO2017068415A1**, *Chemson Polymer-Additive Ag*, Apr. 27, 2017.]

Raw material	Concentration, parts
PVC K=57	100
Titanium dioxide	4
Calcium carbonate	20
Naftosafe CP 3D-Vinyl 70	3.44
Honeywell Rheolub RL-165	0.1
Licowax PE520	0.09
Kaneka PA40	2.94
DINCH	20

Conveyor belt with advertising. [Data from Molinaro, J.; **US Patent 6,971,504**, Dec. 6, 2005.]

Figure 4.29 shows an example of such a conveyor belt which can be used in shops to advertise various products and services. The belting member (16) includes a top surface coating (150) formed of polyvinylchloride. This transparent PVC layer protects the printed surface from wear.

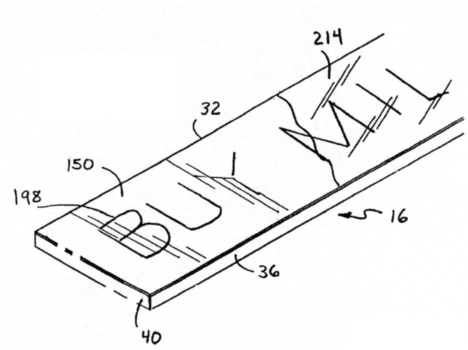

Figure 4.29. Conveyor belt. [Adapted from Molinaro, J.; **US Patent 6,971,504**, Dec. 6, 2005.]

Decorative floor covering. [Data from Son, S.-J.; Jang, H.-S.; Kang, H.-C., **US Patent 6,933,043**, Aug. 23, 2005.]

Raw material	Layer 10	Layer 23
	Concentration, parts	
PVC	100	100
DOP	42	38
Calcium carbonate	250	90
Thermal stabilizer	2	2.5
Titanium dioxide		10

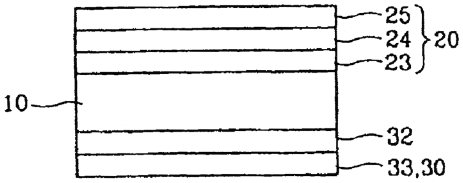

Figure 4.30. Cross-section of decorative floor covering. [Adapted from Son, S.-J.; Jang, H.-S.; Kang, H.-C., **US Patent 6,933,043**, Aug. 23, 2005.]

Figure 4.30 shows a structure of decorative floor covering which contains two PVC layers whose formulations are given in the above table. The cross-sectional view illustrates the structure of the material, in which a polyvinylchloride resin substrate layer (10) is disposed on a decorative floor covering, and a surface layer (20) is disposed on the substrate layer (10). The surface layer (20) can be further subdivided. That is, the surface layer (20) comprises a surface-treated layer (25) on a poly(ethylene terephthalate) film layer (24) and a polyvinylchloride resin intermediate layer (23) under that. The layers below PVC (10) are adhesive layers to bind flooring to the floor. It is clear from this example that the poly(ethylene terephthalate) layer is used here to protect PVC which contains substantial amounts of filler.

Printable billboards. [Data from Spirkovyc, P. A.; Panse, D. R., **US Patent 6,822,024**, Nov.23, 2004.]

Raw material	Concentration, wt%
PVC	49.173
DIDP	20.336
Epoxidized soybean oil	1.230
Calcium carbonate	15.735
Ba/Zn stabilizer (Mark 4848)	0.861
Ba/Zn stabilizer (Mark 4845)	0.861

Printable billboards. [Data from Spirkovyc, P. A.; Panse, D. R., **US Patent 6,822,024**, Nov.23, 2004.]

Raw material	Concentration, wt%
Perchlorate	0.098
Antimony trioxide (flame retardant)	1.967
Acrylic process aid (Paraloid K-175)	0.738
UV stabilizer	0.246
Antioxidant	0.246
Titanium dioxide	7.852
Brightener	0.059
Fungicide (SB-1)	0.600

Advertising information is directly printed on a PVC sheet having the formulation given in the above table.

Inking plate for rotary printing machine. [Data from Fina, R., **US Patent 6.766,741**, Jul. 27, 2004.]

Raw material	Layer 15	Layer 26
	Concentration, parts	
PVC (Hostalit 4472)	1100	1100
PVC (Hostalit 9070)	1100	1250
DOP	1135	1200
Paraplex G54	770	
Monomer X 980		375
Calcium carbonate	825	125
Prosper DBM	45	50
Vinlub 73	10	
Ricardi TPL	10	
Graphite		40

Figure 4.31 shows a cross-section through an inking cylinder carrying a plate according to this invention. It illustrates in a schematic form the inking plate (10) mounted on an inking cylinder (17). The plate (10) comprises the base plate (11), the layer of adhesive (14), and both layers (26) and (15) of PVC, reliefs (16) having been cut into the layer (15). The ends (12) and (13) of the base plate (11) are held in a slot in the cylinder (17) by an appropriate clamping system, e.g., grippers (not shown). The system by which plates are clamped to a cylinder is known in

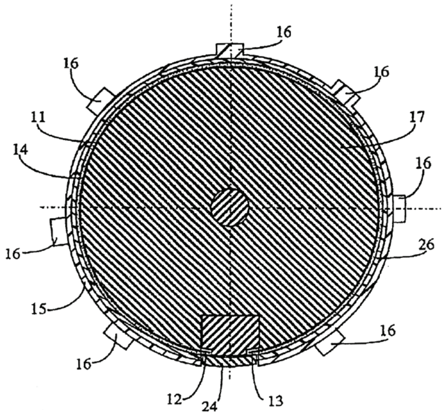

Figure 4.31. The inking cylinder. [Adapted from Fina, R., **US Patent 6.766,741**, Jul. 27, 2004.]

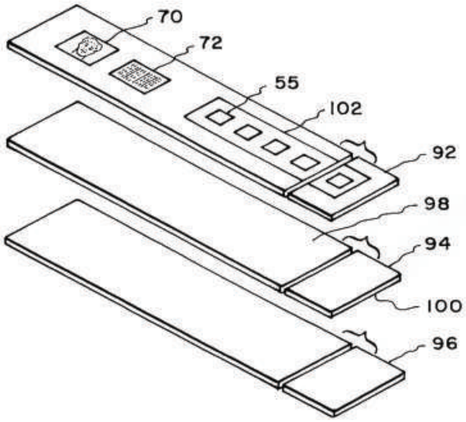

Figure 4.32. Tag structure. [Adapted from Beigel, M. L., **US Patent 5,973,598**, Oct. 26, 1999.]

the field of rotary printing machines. The above table gives formulations of PVC layers. The invention is an example of PVC used in parts of printing machines.

Compressible printing element. [Data from Fountain, R. D., **US Patent 4,388,363**, Jun. 14, 1983.]

Raw material	Concentration, parts
PVC (Geon 121)	100
DOP	60
Phenolic resin (SP6600)	25
Trimethylol propane trimethylacrylate monomer (X980)	15
Thermal stabilizer	3
40% organic peroxide on inert filler (Luperco 231XL)	0.3

Radio frequency identification tag. [Data from Beigel, M. L., **US Patent** 5,973,598, Oct. 26, 1999.]

The tag produces an identification (ID) signal, i.e., a radio frequency (RF) signal carrying identification information, capable of being interpreted by an electronic reader device. A preferred tag is fabricated using a printing process to mark a conductive pattern, e.g., comprised of a conductive ink based on silver, carbon, etc., on a flexible substrate, e.g., polyvinylchloride. In a typical application, the flexible substrate is then preferably used to form a wrist band that can be used to identify an individual to permit, deny or otherwise determine the level of access to an area, e.g., a concert, a work area, or another restricted environment.

Figure 4.32 shows a schematic diagram explaining the structure of such a tag: a laminate of three flexible substrate layers (92,94,96) having conductive, semi-conductive, and insulating polymers imprinted thereon to form organic semiconductors, capacitors, and inductors. A middle flexible substrate layer (94) has polymer patterns printed on its top (98) and bottom (100) surfaces. Conductive ink (55) can be printed or otherwise deposited through the window (102) to programmable encode the signal generator circuitry. Optionally, visually identifiable data can also be printed on the substrate, e.g., a picture (70) and/or a barcoded pattern (72).

Printable self-clinging PVC film. [Data from Nguyen, B. T.; Matsumoto, T.; Katagiri, T., **US Patent 5,698,621**, Dec. 16, 1997.]

Raw material	Concentration, parts
PVC	100
Butyl benzyl phthalate	55
Epoxidized soybean oil	2
Ba/Zn stabilizer	2
Pigment	0.07

On a PVC surface, according to the above formulation, the ink has a very sharp color, good adherence, and fast drying time.

Decorative laminate. [Data from Kauffman, W. J.; Colyer, T. C.; Dees, M., **US Patent 4,950,500**, Aug. 21, 1990.]

Raw material	Base layer	Pigmented layer
	Concentration, parts	
PVC dispersion resin (Tenneco 1732)	100	
PVC dispersion resin (Occidental 605)		100
DOP	35	
Santicizer S-711		34,8
TXIB	17	5
Epoxidized soybean oil	3	2
Tin stabilizer (Mark 275)	1	
Zinc octoate (ABC-18)		1
Azodicarbonamide		1.6
Pigment		0.5-2

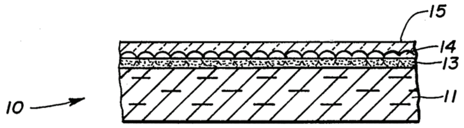

Figure 4.33. Decorative laminate. [Adapted from Kauffman, W. J.; Colyer, T. C.; Dees, M., **US Patent 4,950,500**, Aug. 21, 1990.]

The decorative laminate is used as floor or wall covering. Figure 4.33 illustrates the structure of the decorative laminate (10), which is comprised of a substrate member (11), which is often referred to as a base layer or backing sheet (see formulation in the above table). The substrate member or element (11) bears a layer (12) of foamed PVC resin (see the above table for formulation) disposed preferably over the entire surface of the substrate (11). A layer (13) of PVC resin adhesive is disposed over the entire surface of foamed PVC layer (12). Particles of printed polyvinylchloride (14) are disposed on and secured to the layer (13) of vinyl plastisol adhesive. A top layer (15) of transparent synthetic organic polymeric material overlies the printed PVC resin particles (14). Layer (15) of the laminate (10) is often referred to as a "wear layer" when the laminate is used as a floor covering.

Reticulated PVC plastisol foam. [Data from Lilley, G. L., **US Patent 4,237,239**, Dec. 2, 1980.]

Raw material	Concentration, parts
PVC dispersion resin (FPC 605)	40
PVC dispersion resin (SCC-20)	35
PVC blending resin (Pliovic M-70)	25
DOP	120
Organotin stabilizer (Mark 275)	6.5
PVC dryblend resin particles (PVC 2160)	85
Frothing agent (GE-4254)	8

Oil-based ink for ink-jet printing on PVC. [Data from Sugita, Y.; Tamura, M.; Nakamura, M.; Muchizuki, S.; Otsuki, M., **US Patent 7,125,447**, Oct. 24, 2006.]

Raw material	Concentration, parts
γ-butyrolactone	40
Diethylene glycol	28
Dipropylene glycol monomethyl ether	13
Triethylene glycol monomethyl ether	11
Carbon black	3.5
Dispersant polymer (polyester; Hinoacto KF1-M)	2

Oil-based ink for ink-jet printing on PVC. [Data from Sugita, Y.; Tamura, M.; Nakamura, M.; Muchizuki, S.; Otsuki, M., **US Patent 7,125,447**, Oct. 24, 2006.]

Raw material	Concentration, parts
Binder resin (methyl methacrylate butyl methacrylate copolymer, Paraloid B-99N)	3

The above table gives one of many suitable formulations, all of which contain lactone and polyoxyethylene glycol dialkyl ether solvents in combination with other components of the mixture.

Printing ink. [Data from Day, G. P., **US Patent 6,663,702**, Dec. 16, 2003.]

Raw material	Concentration, wt%
Ethylhexyl acetate	46.83
Ethyl lactate	46.83
Acrylic resin (Elvacite 2021)	0.84
Vinyl copolymer (Ucar VYHH)	1.5
Pigment (Microlith blue 4G-K)	4.0

The above ink-jet ink exhibited excellent adhesion to PVC and dried without a need for external heat.

Water-based ink composition. [Data from Brixius, D. W., **US Patent 4,421,561**, Dec. 20, 1983.]

Raw material	Concentration, parts
Black ink (American ink 18B ink)	100
NH_4OH	55
Azelaic acid	15

Printing ink for foamed PVC. [Data from Hauser, H.; Eckert, P., **US Patent 4,407,882**, Oct. 4, 1983.]

Raw material	Ink	PVC foam
	Concentration, parts	
Pigment preparation (60% pigment and 40% water soluble acrylic resin)	5	
Aqueous alcoholic solution (30-40% water soluble acrylic resin in a form of amine salt; Aquahyde 100)	40	
1-bis(β-hydroxyethyl) aminomethyl benzotriazole	10	
Isopropanol	10	
Water	40-50	
PVC (specific viscosity=0.6)		50
PVC (specific viscosity=0.4)		50
Butyl benzyl phthalate		25
DOP		45
Titanium dioxide		7
Azodicarbonamide		3
Thermal stabilizer		1.5

4.17 ROTATIONAL MOLDING

Rotational molding is a traditional method which has been developed rapidly when good thermal stabilizers became available in the 1940s. Since that time, know-how was developed which is utilized in presently manufactured products. Little technological progress is observed if one considers patent literature on technological developments of PVC rotomolding which is reviewed below in available detail. It should be noted that there is a substantial number of patents available which reveal new developments in machinery used for rotational molding of various polymers.

4.17.1 FORMULATION USED BY RAW MATERIAL SUPPLIER

Buoy-rotomolding. [Data from Eichhloz, H, Martinz D O, **Solvin Paste PVC Handbook**. *Solvay*, 2010.]

Raw material	Concentration, parts
PVC past resin	100
Plasticizer DINP	55
Mineral filler ($CaCO_3$)	10
Stabilizer	2

4.17.2 FORMULATION FOUND IN THE OPEN LITERATURE

Formulation for toys and medical applications. [Data from Wadey, B. L., *J. Vinyl Additive Technol.*, **9**, 4, 172-176, 2003.]

Property	DINCH	DINP
Shore A, 15 sec.	76	74
Shore D, 15 sec.	25	24
Tensile strength, N/m m^2	16.2	16.4
Ultimate elongation, %	355	375
Brittleness temperature, °C	-41	-38
Torsional stiffness, °C	-32	-28
Volatility, 24 hr. @ 130°C	2.4	1.2
Thermal stability, 180°C, min.	19.3	17.5
Compatibility, wt% 28 days 70°C, 100% RH	-0.6	-0.5

Formulation: PVC (K=71) – 100 parts, DINCH or DINP – 60 parts, Ba/Zn stabilizer – 2 parts.
DINCH – di(isononyl) cyclohexane-1.2-dicarboxylate (Hexamoll), DINP – diisononyl phthalate

The formulation is designed for products which require very low toxicity. DINCH is a biodegradable plasticizer. There is no acute toxicological effect after oral or dermal uptake; no skin sensitization in test animals; no indication of genotoxicity; it is not a perisome proliferator; no toxicity to reproduction. In addition, to toys and medical applications, plastisol can be developed for production of gloves by dip coating.

4.17.3 PATENTED INVENTIONS

Rotomolded part. [Data from Fumire, J, **World Patent WO2013092363**, Jan 27, 2013, *Solvay SA*.]

Raw material	Concentration, parts
Solvin 550GA	50
Solvin 250SB	50
Polyethylene wax A-C 316	0.4
Hydrogenated castor oil Loxiol G15	2
Acrylic process aid Paraloid K-175	0.4
Organotin stabilizer Advastab TM-181 FS	3.5
Epoxidized soybean oil	4
Diisononyl phthalate	5
Paraffin Vestowax SH 105	0.1
Silica Sipernat 310	0.5
Ultramarine blue	0.01

Rotomolded toy. [Data from Godwin, A D, Gosse C, **European Patent EP2358801**, Aug. 24, 2011, *ExxonMobil Chemical Patents, Inc*.]

Raw material	Concentration, parts
PVC	100
Di-C7 terephthalate	40
TXIB	20
$CaCO_3$	5
Stabilizer	2.5
Epoxidized soybean oil	3

Composition for rotational molding. [Data from Igarashi, T.; Wakatsuki, A.; Shida, Y., **US Patent 5,310,805**, May 10, 1994.]

Raw materials	Concentration, parts
PVC (polymerization degree=3600; particle size=1 μm)	103
DOP	60
Epoxidized soybean oil	4
Ca/Zn stabilizer	3
Pigment	q. s.

Three main parameters of dry blend preparation were controlled: powder flowability, pinhole formation, and antiblocking property. They are influenced by the formulation, especially by the selection of PVC which must have high polymerization degree and by its particle size. The technology of dry blend preparation was also found important. It included the following steps: first, the resin was added and mixed until the temperature reached 80°C, then all other ingredients were added and mixing continued until the temperature has reached 120°C. At this point, dry blend was cooled to 50°C, and 3 parts by weight of PVC were added and uniformly dispersed to improve flowability.

Composition for rotational molding. [Data from Isao, M.; Kobayashi, M.; Wakatsuki, A., **US Patent 4,659,764**, Apr. 21, 1987.]

Raw material	Concentration, parts
S-PVC (polymerization degree=700)	2000
Microsuspension PVC	200
Barium octoate	25
Zinc octoate	25
Epoxidized soybean oil	70
Gray pigment	105
Thioether antioxidant	3
UV absorber	2
Trioctyl trimellitate	1400

Flowability, mold staining, thermal stability and UV resistance, and transparency were the primary control parameters for quality purposes. The following technology of dry mixture preparation was used: first suspension PVC was added to the mixer, followed by addition of a dispersion of all minor additives in 400 parts of plasticizer, after mixing remaining plasticizer (1000 parts) was added, and the mixture mixed until powder became dry (plasticizer fully absorbed). After cooling, microsuspension PVC was thoroughly mixed in to make material flowable.

Phthalate-free rotomolded toys. [Data from Buess, P, Caers, R F, Colle, K S, Godwin, A, Saleh, R Y, Stanat, J E R, Less, D, **European Patent EP2268727**, Jan. 5, 2011, *ExxonMobil Chemical Patents Inc.*]

Raw material	Concentration, parts
S-PVC	100
Polyol ester plasticizer (this invention)	30
Palatinol DINCH	40
Filler	20
Stabilizer	3
Other additives	3

Balancing device. [Data from Weck, D.; Cotter, J. E. E., **US Patent 7,344,488**, Mar. 18, 2008.]

Figure 4.34 shows an inflatable device used for fitness purposes to maintain balance and equilibrium. The patent gives details of construction and production of such a device from flexible PVC. No formulation is given in the patent.

Watercraft fender. [Data from DeRuscio, J. C., **US Patent 6,021,729**, Feb. 8, 2000.]

Figure 4.35 shows another example of a patented product from PVC suggested for manufacture by rotational molding. The fender (10) is composed of PVC pipe obtained by extrusion and attachment members made by rotational molding.

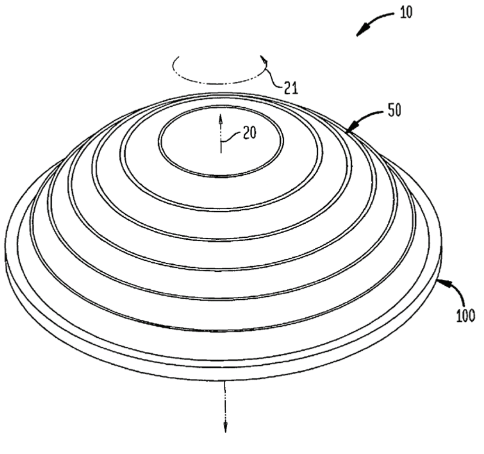

Figure 4.34. Balancing device. [Adapted from Weck, D.; Cotter, J. E. E., **US Patent 7,344,488**, Mar. 18, 2008.]

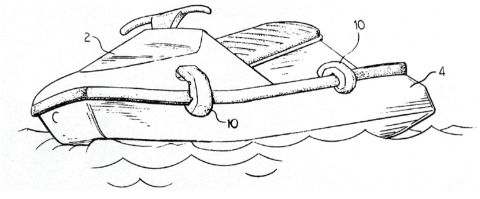

Figure 4.35. Watercraft fender. [Adapted from DeRuscio, J. C., **US Patent 6,021,729**, Feb. 8, 2000.]

4.17.3 CONCLUSIVE REMARKS

Typical formulations for rotational molding are simple. Plastisols, “drysols”, and micropellets are typical forms of precompounded material used in rotational molding. “Drysols”, similar in concept to dry blends and micropellets, are precompounded in an extruder and extruded in the form of micropellets. Micropellets permit use of higher molecular weight PVC for soft articles which cannot be used in dry blend form since high molecular weight PVC requires a more plasticizer to make it soft and flexible and the addition of this amount of plasticizer will produce a sticky powder. In addition to raw materials mentioned in the above tables, lubricants, antioxidants, UV stabilizers, flame retardants, crosslinking agents, and blowing agents are also used when required.

Flowability of the liquid or particulate premix is the most critical feature of formulation which determines product properties, thickness uniformity, and frequently product appearance.

Several troubleshooting hints are related to the formulation. They include:

- long oven cycle (too low melt index of polymer, sticky additives, or too fine particles)
- unfused parts (selection of plasticizers, too coarse particles)
- degradation (insufficient stabilization)
- poor impact strength (polymer molecular weight, the addition of impact modifier, pigment interferes with crystallization)
- part sticks to mold (release agent required)
- the surface defect, wall thickness non-uniform (too high viscosity of the mixture, too low melt flow)
- bubbles (excessive moisture, volatile compounds in the mixture, degradation products)
- flash in parting line (melt flow index to high)

4.18 SEALANTS

4.18.1 FORMULATIONS PROPOSED BY THE RAW MATERIAL SUPPLIERS

Automotive mastic. [Data from Eichhloz, H, Martinz D O, **Solvin Paste PVC Handbook**. *Solvay*, 2010.]

Raw material	Concentration, parts
PVC paste resin	80
PVC blending resin	20
Plasticizer DINP	150
Mineral filler ($CaCO_3$ 5 µm)	100

PVC plastisol sealant formulation. [Data from *Specialty Minerals*, 2013.]

Raw material	Concentration, wt%
PVC	19
Plasticizer	34
Precipitated calcium carbonate (Ultra-Plex PCC)	26
Ground calcium carbonate (Vicron 25-11 GCC)	14
Diluent	4
Desiccant (CaO)	2
Adhesion promoter	0.5

4.18.2 PATENTED INVENTIONS

Flame retardant plastisol as sealant or backing. [Data from Papazoglou, E S, Malin, K R, Papathomas, C J, **US Patent US20120282432**, Nov. 8, 2012, *Polymer Products Company, Inc.*]

Raw material	Concentration, parts
PVC	79
Zeolite	3
Alumina trihydrate	10
Calcium carbonate	5
Phosphate plasticizer	3

PVC underbody sealant. [Data from Godwin, A D, Gosse C, **European Patent EP2358801**, Aug. 24, 2011, *ExxonMobil Chemical Patents, Inc*.]

Raw material	Concentration, parts
PVC (homo or copolymer)	100
Di-C7 terephthalate ester	80-120
$CaCO_3$	80-120

Glue for articles made of PVC [Data from Beuer, B.; Beck, H.; Trauten, R., **EP2687571B1**, *Henkel AG and Co KGaA*, Dec. 10, 2014.]

Raw material	Concentration, wt%
2-Methyltetrahydrofuran	29
Butane-2-one	26
Cyclohexanone	23.39
Aerosil 200	1.5
PVC	20
Calcium stearate	0.1
NH_4CO_3	0.01

Glue composition comprising the solvent N-acetylmorpholine

[Data from Jensen, M., **US20130096242A1**, *Nordcoll AS*, Apr. 18, 2013.]

Raw material	Concentration, wt%
N-Metyl-pyrrollidone	4.5
N-Ethyl-pyrrollidone	71.5
N-Acetylmorpholine	4.5
Ca/Zn stabilizer	0.128
Silicon dioxide (thixotropic agent)	3.229
PVC (Vinnolit S3368D)	16.145

4.19 SINTERING

This is another technique used less frequently, but some patents can be found on this subject, and these are reported below.

4.19.1 PATENTED INVENTIONS

Microporous material. [Data from Rainer, N. B., **US Patent 6,569,495**, May 27, 2003.]

Raw material	Concentration, parts
Anhydrous glycerin	90
PVC emulsion (Vycar 351 (57.9 PVC))	150
Cellulose sponge cubes (1/2" size)	34.7

The mixture of glycerin and PVC emulsion is wholly absorbed by sponge cubes, which are further tumbled to achieve uniform distribution of liquid. The impregnated cubes are exposed to 100°C for 30 min and at 127°C for 40 min, which is sufficient to sinter particles of PVC. Glycerin is washed out by water in the next step and cubes are dried. Cubes have a PVC/cellulose ratio of 3.41/1, and they have a microporous structure. The cubes are used to remove toxic organic species from water such as polychlorinated biphenyls, dioxins, polyaromatic hydrocarbons, nitroaromatics, pesticides, herbicides, and volatile halocarbons.

Dust-free PVC. [Data from DiRienzo, D. J., **US Patent 5,155,185**, Oct. 13, 1992.]

Raw material	Concentration, parts
PVC (Geon 143)	100
Dust-free mass resin	9
DIDP	45
Epoxidized soybean oil	5
Tin stabilizer (Mark 190)	4

This patent reports on special PVC developed by BFGoodrich (now PolyOne). Mass polymerized resins are suitable in some application, including sintering, for which the above formulation was used. Sintering process took 5 min at 232°C.

Battery separators. [Data from Riesberg, V.V., **US Patent 4,252,756**, Feb. 24, 1981.]

The goal of this invention is to produce battery separators which have a porosity higher than 50%. This porosity is required for electrolytic processes to occur. The goal is achieved by mixing PVC powder with a pore-forming substance (e.g., 5% $NaHCO_3$) which, during the process of sintering at temperatures as high as 230°C, undergoes degradation with the formation of gas which helps to form the required porosity. The technology and equipment are fully disclosed in the patent.

4.20 SLUSH MOLDING

Slush molding is a similar molding technique to dip molding used in PVC processing. The difference is that plastisol is poured into the mold (in dip molding the mold is inserted into a plastisol), and the mold is heated to gel and fuse plastisol. Some examples of inventions are discussed below.

4.20.1 PATENTED INVENTIONS

Air bag doors (low VOC and fog). Tansey, W J, **US Patent US20110028625**, Feb. 3, 2011, *International Automotive Components Group North America, Inc.*]

Raw material	Concentration, wt%
Geon 471	44.1
Palatinol 610TM	38.8
Plasthall CF	9.7
Formolon 24-A	3.1
Therm-Chek 1187	1.8
Tinuvin XT 833	0.22
Stearic acid	0.04
Color	2

Earplugs. [Data from Turor, M. S.; Green, R. W., **US Patent 6,129,175**, Oct. 10, 2000.]

Raw material	A	B
	Concentration, parts	
PVC	100	100
DOA	400	470
DOP	70	
Epoxidized soybean oil	10	10
Ca/Zn stabilizer	10	10
Pigment	q.s.	q.s.

Earplugs have a noise reduction rating from 20 to 36 dB.

Vinyl chloride resin composition for powder slush molding [Data from Iwahori, T.; Kitagawa, Y., **US20150322244A1**, *Zeon Corp*, Nov. 12, 2015.]

Raw material	Concentration, parts
PVC (Zest1700Z)	100
Trimellitate plasticizer (Trimex N-08)	115
Epoxidized soybean oil	5
Zeolite (Mizukalizer DS)	1
Stearoylbenzoylmethane (Karentz DK-1)	0.3
Oxidation inhibitor (Irganox 101)	1
Ultraviolet stabilizer (Tinuvin P)	0.3
Light stabilizer (Adeka Stab LA-67)	0.2
Release agent (zinc stearate)	0.2
Release agent (12-hydroxy stearic acid)	0.4
Dusting agent	20
Pigment (carbon black)	5

Vinyl chloride resin composition for powder slush molding [Data from Nishimura, S., **EP3266826A4**, *Zeon Corp*, Sep. 5, 2018.]

Raw material	Concentration, parts
PVC (Zest2500Z)	100
Trimellitate plasticizer (Trimex N-08)	110
Epoxidized soybean oil	5
Perchloric acid treated hydrotalcite (Alcamizer 5)	4.56
Zeolite (Mizukalizer DS)	2.42
Stearoylbenzoylmethane (Karentz DK-1)	0.49
Oxidation inhibitor (Irganox 101)	1
Phosphite antioxidant	0.6
Light stabilizer (Adeka Stab LA-67)	0.2
Release agent (zinc stearate)	0.2
Release agent (12-hydroxy stearic acid)	0.4
Silicon oil (viscosity 10^4 cs) (KF-96H)	1.5
Dusting agent	20
Pigment (carbon black)	3.7

Slush molding formulation of plastisol (A) and powder (B). [Data from Ngoc, H. D., **US Patent 5,840,236**, Nov. 24, 1998.]

Raw material	A	B
	Concentration, parts	
PVC	100	100
Highly crosslinked nitrile rubber	20	
Free-flowing NBR powder		12
Antioxidant (Wingstay K)	0.2	0.2
DOP	85	50
Thermal stabilizer	3	3

Traffic channelizer base. [Data from Monda, A. F.; Hinnant, M. D., **US Patent 5,795,530**, Aug. 18, 1998.]

Raw material	Concentration, parts
Off-grade PVC	5.4
DOP	6.75
Barium sulfate	11.80
Pigment (Austin black)	0.54
Desiccant (calcium oxide)	0.11
Viscosity modifier (mineral spirits)	0.42

Traffic channelizers are used on roadways to warn motorists of road hazards and to direct traffic along the desired route. For example, a series of traffic channelizers may be positioned one after another along the roadway to channel traffic in a construction zone into fewer lanes.

Higher than 1.25 density is required to make the base stable against wind forces and vacuum forces created by passing vehicles. This was achieved by using the slush molding process and formulation given in the above table.

4.21 SOLVENT CASTING

In the current state of environmental protection, any solvent casting is not a viable technological option. Also, PVC is not an ideal polymer for solvent casting because it forms very viscous solutions with the majority of good solvents. This does not preclude outstanding cases of use. In the case of PVC, sensor membranes are these exceptional examples of application of solvent casting in PVC processing.

4.21.1 PATENTED INVENTIONS

Sensor device. [Data from Vadgama, P. M.; Christi, I. M.; Benmakroha, Y. M.; Reddy, S. M., **US Patent 5,567,290**, Oct. 22, 1996.]

The PVC membrane described in this patent acts as a barrier to paracetamol and sugars, but it is permeable to hydrogen peroxide. The membrane is used to detect the activity of enzyme oxidase which readily forms hydrogen peroxide from glucose. The membrane is made from pure PVC (no additives or plasticizers) by solvent casting to obtain a thickness of 10 to 40 μm.

Sensor membrane. [Data from Clausen, L., **US Patent 7,195,697**, Mar. 27, 2007.]

This membrane is designed for a sensor which has a layered structure. The sensor can measure glucose, lactate, urea, and creatinine. The membrane is composed of a polymer, surfactant, and hydrophylic compound. Upon conditioning, the membrane structure includes a system of pores which give the membrane excellent permeability.

Soil chemistry sensor [Data from Miller, T.; le Besnerais, P-H; Malaurie, H., **WO2014096844A1**, *Plant Bioscience Limited*, Jun. 26, 2014.]

Raw material	Concentration, wt%
Tridodecylmethylammonium nitrate	1.5
2-Nitrophenyl octyl ether	16.25
Nitrocellulose, 35% in isopropanol	1.93
Methyltriphenylphosphonium bromide	0.25
Polyvinyl chloride) high molecular weight	5.75
Tetrahydrofuran	74.32

4.22 SPRAYING

Intuitively, it can be anticipated that PVC will not be a material of choice to be processed by spraying because in any used form it has too high a viscosity. But there are some cases reported below where PVC in some half ready form is processed by being sprayed by another material. But there is also one case reported of a product manufactured by spraying PVC plastigel.

4.22.1 PATENTED INVENTIONS

Spray molded article. [Data from Tresino, J, Cassata, B, Horton, S D, **European Patent EP2646498**, Oct. 9, 2013, *PolyOne Corporation*.]

Raw material	Concentration, wt%
Low fog PVC	46.93
Low fog BaZn stabilizer	3.75
Amine scavenger	0.47
Low temperature trimellitate plasticizer	30.03
Polyol mold release	1.88
Low temperature sebacate plasticizer	9.85
UV stabilizer	2.35
Epoxidized soybean oil	4.69
Fumed silica thickener	0.05

Spray-coated gloves. [Data from Ahmed, S U, Ahmed, R R, Kassim, M, **European Patent EP2527123**, Nov. 28, 2012, *Midas Safety*.]

Raw material	Concentration, parts
Pevikon P737 (past-making PVC)	83
PVC SPRD (VC/VAc copolymer, blending resin)	17
Palatinol AH (DOP	96.87
Santicizer 160 (BBP)	19.8
Calcium stearate (heat stabilizer)	2
Mark 1495C (heat stabilizer)	1.5
Epoxidized soybean oil	5
Aerosil 200 (thickener)	0.1
Agitan 6236M (antifoam)	0.1
Pigment	0.83

Doormat. [Data from Wang, H. L., **US Patent 7,276,133**, Oct. 2, 2007.]

The doormat is produced using the following steps: first, a PVC loop mat is prepared, which is then adhered to a substrate. The PVC loop mat is then sprayed with paint to form a desired picture on its surface.

Heat-proof laminate board. [Data from Lin, G., **US Patent 5,612,111**, Mar.18, 1997.]

The heat-proof laminate board is produced from corrugated steel plate (forming the surface of the laminate) and PVC sheet which is sprayed on the surface with foaming polyurethane, which fills space between two plates and glues them together.

Flexible shell. [Data from Bertrandi, L., **US Patent 4,122,146**, Oct. 24, 1978.]

Raw material	Concentration, parts
PVC	100
DOS	15
Trimellitate	35
Thermal stabilizer	2.5
Epoxidized soybean oil	3
Titanium dioxide	2
Bentonite (geller)	2
Viscosity depressant	2

The above plastigel has a viscosity of 35,000 cps. Its viscosity increases to 160,000 cps during the first 24 h. Plastigel is sprayed on the surface of the mold and baked until complete fusion occurs. Several details are missing from this formulation.

4.23 THERMOFORMING

4.23.1 FORMULATION FOUND IN THE OPEN LITERATURE

PVC-wood fiber composite. [Data from Matuana, L. M.; Kamdem, D. P.; Zhang, J., *J. Appl. Polym. Sci.*, **80**, 11, 1943-1950, 2001.]

Raw material	Concentration, parts
PVC (K=57)	100
Tin stabilizer (PlastiStab)	2
Calcium stearate (Synpro)	1.2
Paraffin wax (Gulf Wax)	1
Process aid (Paraloid K-120)	1.2
Process aid (Paraloid K-175)	1
Wood fibers	30
Aminosilane	1.5
Pigment (TiO_2)	0-10

Wood fibers were found to be effective sensitizers of UV degradation. It is thus essential to protect composite by addition of photoactive pigment such as titanium dioxide.

4.23.2 PATENTED INVENTIONS

PVC thermoforming composition [Data from Schuessler, S.; Weiss, A.; Wewior, G.; Giersbach, F., **US20150000782A1**, *George Fischer DEKA GmbH*, Jan. 1, 2015.

Raw material	Concentration, parts
PVC	48
CPVC	52
Tin stabilizer	0.5
Titanium dioxide	0.1
Pigment	0.65
Oxidized PE	1
Acrylic gelling and processing aid	1
Antioxidant	1

Biodegradable film for pharmaceutical packaging. [Data from Klaus, W M, Marco, P, Ajith, S N, Naik, P, **World Patent WO2013076734**, May 30, 2013, *Bilcare Ltd*.]

Raw material	Concentration, parts
PVC	255.7
VC/VAc copolymer	49.90
Methylmethacrylate-butadiene-styrene terpolymer	14.52
PVC emulsion polymer	39.50
Polyol ester-based lubricant	1.5
Amide of ethylenediamine	0.5
Acrylic process aid	2.06
Butadiene-methacrylate-styrene	2.42
Bio pro-degradant (Eco-pure)	4
Titanium dioxide	1.4
Thermal stabilizer	3.75
Partial ester of fatty acid	3.04

PVC for manufacturing sterilizable containers [Data from Toscano, M.; Zanichelli, A., **WO2014076717A1**, *Resilia S.r.l.*, May, 22, 2014.]

Raw material	Concentration, parts
PVC	75-90
Organic phosphitic esters	0.1-1
Epoxidized soybean oil	1-5
Tin mercaptide	1-5
Thioglycolic acid derivative	0.35-5
Acrylic/methacrylic copolymer	5-20
Polyhydric alcohol	0.2-2
PE wax	0.01-0.2
Stearamide	0.1-0.5

Multiple pipette sampler system. [Data from Hanaway, R. W.; Hrudicka, J., **US Patent 5,348,606**, Sep. 20, 1994.]

Figure 4.36 shows an array of cavities (14) formed downwardly from an integral flat sheet (16). A precision die is used to thermoform a 0.015 to 0.020 inch polyvinylchloride plastic sheet so that each cavity (14) is identical. The tip of each pipette cavity (14) is removed so that a liquid may be drawn into the cavity.

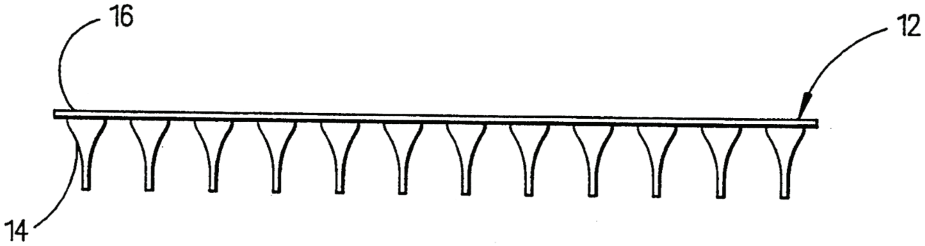

Figure 4.36. Pipette array. [Adapted from Hanaway, R. W.; Hrudicka, J., **US Patent 5,348,606**, Sep. 20, 1994.]

Multilayer interliner for refrigerators in contact with HCFC chemicals.

[Data from Greenlee, W. S., **US Patent 5,248,546**, Sep. 28, 1993.]

Raw material	A	B
	Concentration, parts	
PVC (inherent viscosity=0.68; e.g. Geon 86)	100	100
Paraloid K-120N	2	2
Acrylic imide (Paraloid HT-510)		50
Epoxidized soybean oil	3	1
Thermal stabilizer	2	3
Glycerol monostearate	1	1
Acrylic (Durastrength 200)	2	6
Acrylic impact modifier	6	5
MBS impact modifier	8	
Oxidized PE		0.4
Mineral oil	3.8	
Stearic acid		2.2

The article has 3 layers A-B-A. The layer B is so designed that it has heat distortion temperature higher by at least 3°C than layer A (in the example given in the table, heat distortion temperatures for A and B are 68 and 83°C, respectively). The multilayer laminate is produced by coextrusion and shaped by thermoforming.

4.24 WEB COATING

4.24.1 GENERAL

4.24.1 Formulations given by raw material suppliers

Wear layer (transparent top layer). [Data from Eichhloz, H, Martinz D O, **Solvin Paste PVC Handbook**. *Solvay*, 2010.]

Raw material	Concentration, parts
PVC	100
Plasticizer DINP	45
Viscosity depressant	5
Stabilizer (CaZn)	2.5

Lower cost plastisol formulation [Data from Eastman formulation additive technical tip, TT-32B, 2006.]

Raw material	Concentration, parts
Oxy 654 P_VC	100
Eastman 168 plasticizer	38
Eastman TXIB	12
Akrostab LT 4798	3
Hubercarb 325	40

4.24.2 Patented inventions

New plasticizer. [Data from Kayten, H., **US Patent 7,411,012**, Aug. 12, 2008.]

Raw material	A	B	C	D
	Concentration, parts			
PVC (Solvin 271)	100	100	100	100
Diisononyl phthalate	60			
N-dodecyl-2-pyrrolidone (new plasticizer, Surfadone LP 300)		20	40	60
Baerostab CT 9156X (Ca/Zn stabilizer)	2.5	2.5	2.5	2.5
Shore A hardness	77	96	77	63
Tensile strength, N/mm^2	20.0	23.5	11.8	6.8
Elongation at break, %	136	79	94	117

Effect of benzoates. [Data from Grass, M.; Koch, J., **US Patent 7,323,588**, Jan. 29, 2008.]

Raw material	A	B	C
	Concentration, parts		
E-PVC (Vestolit B 7021)	100	100	100
Isononyl benzoate	50		
2-ethylhexyl benzoate		50	
2,5,5-trimethylhexyl benzoate			50
Costabilizer (Drapex 39)	3	3	3
Stabilizer (Mark CZ 140)	1.5	1.5	1.5
Weight loss 200°C (thermogravimetry with temperature rise of 10°C/min), %	24.3	31.8	90.6
Plastisol viscosity after 7 days, Pas	1.39	2.63	0.99
Glass transition temperature (plastisol), °C	-49	-47	-39

New plasticizers. [Data from Lang, J.; Stanhope, B. E.; Bohnert, T. J.; Arendt, W. D., **US Patent 6,933,337**, Aug. 23, 2005.]

Raw material	DEG3BL*	DEG9BL**	DOP
	Concentration, parts		
PVC	100	100	100
Plasticizer (different as indicated in labels)	55	55	55
2,2,4-trimethylpentane diisobutyrate	3	3	3
Epoxidized soybean oil	4	4	4
Ca/Zn stabilizer (Irgastab CZ 116)	3	3	3
Viscosity of plastisol, Pas	1.1	1.6	1.8
Gelation temperature, °C	67	65	76
Freezing temperature, °C	5	-15	
Weight loss at 190°C/3 h, %	55.4	60	95.7

*DEG3BL = ester of diethylene glycol and a mixture of benzoic and lauric acids in the proportion of 3:1

**DEG9BL = ester of diethylene glycol and a mixture of benzoic and lauric acids in the proportion of 9:1

Effect of PVC particle size. [Data from Saethre, B.; Pedersen, S., **US Patent 6,441,085**, Aug. 27, 2002.]

Raw material	A	B	C	D	E
	Concentration, parts				
PVC A	100	95	80	65	30
PVC B	0	5	20	35	70
DOP	50	50	50	50	50
Epoxidized soybean oil	2	2	2	2	2
Thermal stabilizer (LZ616)	2	2	2	2	2
Brookfield viscosity at 2.5 rpm, Pas	8.1	6.6	4.0	3.3	8.8
Brookfield viscosity at 20 rpm, Pas	6.1	5.3	3.7	3.5	8.9
Haake at 400 s^{-1}, Pas	11.8	9.4	5.5	4.3	6.0
Gloss, %	42		55	40	31

Polymer A had a particle size of 0.6 μm and polymer B a particle size of 22 μm. It is evident from this study that mixing larger and smaller particles in proper proportions reduces viscosity and can even improve gloss. Both phenomena are due to better packing of particles of different sizes.

Adhesion promoters. [Data from Van de Berg, A.; Fitzek, D., **US Patent 6,040,385**, Mar. 21, 2000.]

Raw material	A	B
	Concentration, parts	
PVC (K=70)	100	100
DOP	125	125
Chalk	80	80
Tribasic lead sulfate	3	3
Polyimidoamine based on olefin/maleic anhydride copolymer and N-aminoethylpiperazine	0.5	
Polyimidoamine based on olefin/maleic anhydride copolymer and dimethylaminopropylamine		0.5
Adhesive strength (BASF KTL metal plate)	4 (maximum strength)	
Yellowness index at 160°C (control YI=20)	44	46

The patent contains methods of synthesis of both adhesion promoters.

Acidic adhesion promoters. [Data from Huynh-Tran, T.-C., **US Patent 5,032,432**, Jul. 16, 1991.]

Raw material	A	B
	Concentration, parts	
PVC	25	
PVC copolymer (5 wt% VAc)		25
Diglycidyl cycloaliphatic epoxy resin	12.5	
Diisodecyl phthalate	25	
Diisononyl phthalate		20
Calcium carbonate	32.5	38
Succinimide		4.9
Polyadipic polyanhydride		0.4
Calcium oxide		2
N-ethyl o/p-toluenesulfonamide		5
Bisphenol A epoxy resin diluted with 15 wt% C12-C14 aliphatic glycidyl ether		3
Maleic anhydride	5	1.7

Both plastisols have excellent adhesion to coatings and metals. Plastisol B is storage stable.

Flame-retarding system. [Data from Catone, D. L.; Kinsman, M. A., **US Patent 5,863,967**, Jan. 26, 1999.]

Raw material	Concentration, parts
PVC (Geon 121)	100
Phthalate plasticizer (Santicizer 711)	50
Sb_2O_5 powder (Nyacol A1588LP)	2.5
Epoxidized soybean oil (Plas-Chek 775)	5
Ba/Zn stabilizer (Therm-Chek 1159-SF)	3

The flame retardant used in the formulation given in the above table was found to not affect the action of thermal stabilizer and clarity of material.

Light-weight plastisol. [Data from Gerace, M. J., **US Patent 5,658,969**, Aug. 19, 1997.]

Raw material	Concentration, parts
PVC	32.5
Diisononyl phthalate	48.1
Hollow thermoplastic microspheres (Dualite M6032AE)	12
Fluoroaliphatic non-ionic surfactant (Fluorad FC-430)	1.2
Calcium oxide	2.4
Titanium dioxide	1.2
Stabilizer (Interstab CZ)	0.6
Amidoamine resin (Versamid 66)	1.2
Fume silica	0.6
Slump, mm	1
Tensile strength, psi	145
Elongation, %	105
Specific gravity (initial)	0.61
Specific gravity (pumped)	0.64
Pumping flow rate, g/s	1.1

The development of hollow thermoplastic microspheres has offered the prospect of plastisols having lower density with superior physical properties and appearance not attainable by other known techniques. Such microspheres have become available, having, for example, diameters on the order of 10 to 200 µm, most often 20 to 100 µm, and densities of 0.06 to 0.02 g/cm^2, or even as low as 0.015 g/cm^2. The thermoplastic material of which the microspheres are formed is typically a polyvinylidene chloride or a copolymer of polyvinylidene chloride with other vinyl or acrylic monomers, such as acrylonitrile, butylene, and the like. The hollow microspheres contain a physical blowing agent, typically a lower alkane, most often a butane or pentane, or their mixtures. A variety of such materials are commercially available.

Method of plastisol manufacture and use determines final product density. Formulation of a plastisol composition comprising a thermoplastic resin, a plasticizer resin, inert filler, and hollow thermoplastic microspheres should consider the following points:

- the thermoplastic microspheres must be coated with a surfactant which wets the surface of the microspheres, in an amount sufficient to substantially or entirely coat the surface of the microspheres

- combining the microspheres and the optional inert filler into the plastisol formulation in a proportion which does not exceed the critical pigment volume concentration of the plastisol
- mixing and pumping formulation at the lowest effective temperatures and pressures required to produce and apply the plastisol composition

PVC/PU blend. [Data from Petit, D.; Ladang, M., **US Patent 5,428,087**, Jun. 27, 1995.]

Raw material	PVC	PVC/PU
	Concentration, parts	
PVC (Solvic 372HA)	100	100
Tricresyl phosphate	90	90
Epoxidized soybean oil	10	10
Thermal stabilizer	0.5	0.5
Polyol (poly-ε-caprolactone, CAPA 316)	0	48
Isocyanate (IPDI)	0	52
Catalyst (tin dibutyldilauryl sulfate, Dabco T12)	0	0.5
Retention of tensile strength at 100°C in %	9.3	14.3
Retention of 50% modulus at 5% elongation at 100°C in %	11.7	24.4
Creep resistance, mm	314	115
Gel content, %	0	30

Blending PVC with crosslinkable polyurethane components improves resistance to heat and solvent and reduces plasticizer migration.

Use of optical brighteners. [Data from Briti, M. J.; Garcia, F. J., **US Patent 5,205,963**, Apr. 27, 1993.]

Raw material	Control	A	B
	Concentration, parts		
PVC	8	8	8
PVC copolymer	5	5	5
Diisononyl phthalate	28	28	28
Polyaminoamide	2	2	2
Ground chalk	39	39	39
Precipitated chalk surface coated	13	13	13
Titanium dioxide	2	2	2
Calcium oxide	3	3	3

Use of optical brighteners. [Data from Briti, M. J.; Garcia, F. J., **US Patent 5,205,963**, Apr. 27, 1993.]

Raw material	Control	A	B
	Concentration, parts		
Optical brightener (Uvitex OB)		300 ppm	
Optical brightener (Leucopur EGM)			300 ppm
Δb freshly baked	1	0	-0.75
Δb after 8 weeks aging at 80°C	3	2.2	2.1

Expandable plastisol. [Data from Preat, J.-L., **US Patent 4,931,478**, Jun. 5, 1990.]

Raw material	A	B
	Concentration, parts	
PVC	100	25
PVC copolymer (4 wt% VAc)		75
DOP	70	60
Benzyl butyl phthalate		10
Calcium carbonate	25	50
Titanium dioxide	3	
Azodicarbonamide	3	1.7
Zinc chloride (5 parts of zinc chloride and 3 parts of water)	0.4	0.8

Introduction of additives into already manufactured product. [Data from Gasman, R. C., **US Patent 4,728,540**, Mar. 1, 1988.]

Raw material	UV stabilizer	Mildewcide	Stabilizers
	Concentration		
UV absorber (2-ethylhexyl-2-cyano-3,3-diphenyl acrylate)	1 phr		
Plasticizer (2,2,4-trimethyl-1,3-pentanediol diisobutyrate)	2 g	2 g	45 wt%
Mildewcide (45% 2-n-octyl-4-isothiazolin-3-one in dipropylene glycol)		1 phr	
Ba/Cd stabilizer (now obsolete)			2 wt%
Epoxidized soybean oil			5 wt%
Triphenyl phosphite			1

Introduction of additives into already manufactured product. [Data from Gasman, R. C., **US Patent 4,728,540**, Mar. 1, 1988.]

Raw material	UV stabilizer	Mildewcide	Stabilizers
	Concentration		
2-hydroxy-4-n-octoxybenzophenone			1
Absorption time (room temp), h	47	16	288

Compositions were applied to material surface which was left to absorb an additive dispersed in plasticizer.

4.24.2 COATED FABRICS

4.24.2.1 Formulations proposed by the raw material suppliers

Top layer formulation. [Data from Eichhloz, H, Martinz D O, **Solvin Paste PVC Handbook**. *Solvay*, 2010.]

Raw material	Concentration, parts
PVC	100
Plasticizer DINP	80
Epoxidized soybean oil	4
Stabilizer (BaZn)	2

Spread-coating compound. [Data from **Mark RFD**. Technical data sheet. *Chemtura*.]

Raw material	Concentration, parts
PVC (dispersion grade)	100
Phthalate plasticizer	60
Drapex 4.4	5-10
Filler	0-20
Mark RFD (liquid Ba/Zn stabilizer)	1.5-3

Automotive artificial leather. Foam layer. [Data from Eichhloz, H, Martinz D O, **Solvin Paste PVC Handbook**. *Solvay*, 2010.]

Raw material	Concentration, parts
PVC	100
Linear 9-11 phthalates	60
Blowing agent and solid kicker	3

Automotive artificial layer. Solid layer. [Data from Eichhloz, H, Martinz D O, **Solvin Paste PVC Handbook**. *Solvay*, 2010.]

Raw material	Concentration, parts
PVC	100
Palatinol 911	60
Ca/Zn/Al stabilizer	4

Artificial leather. Soft foam. [Data from Eichhloz, H, Martinz D O, **Solvin Paste PVC Handbook**. *Solvay*, 2010.]

Raw material	Concentration, parts
PVC	100
Plasticizer DINP	90
Mineral filler ($CaCO_3$ 10 mm)	20
Blowing agent (ADCM)	2
Kicker	2

4.24.2.2 Formulation found in the open literature

Leathercloth. [Data from Arendt, W. D.; Lang, J., *J. Vinyl Additive Technol.*, **4**, 3, 184-188, 1998.]

Raw material	Top coat	Foam layer
	Concentration, parts	
PVC dispersion resin	100	100
Plasticizer	65	75
Epoxidized soybean oil	5	5
Carboxylic acid derivative	5	
Azodicarbonamide		2
Calcium carbonate	15	
Zinc oxide		0.8
Ba/Zn stabilizer	3	1.5
Titanium dioxide		3

4.24.2.3 Patented inventions

Plastisol formulation (an alternative method of stabilization). [Data from Krainer, E.; Bacaloglu, R.; Shah, M.; Fisch, M. H.; Frenkel, P.; Bae, K. J., **US Patent 7,282,527**, Oct. 16, 2007.]

Raw material	Concentration, parts
PVC (Geon 129)	100
Diisononyl phthalate	70
Drapex 6.8	5
Polyethylene glycol 200	0.47
Epoxy resin (GY-250)	2
60% solution of sodium perchlorate	0.33

Coated fabric for tenting. [Data from McKinney, J. M.; Hodson, J. G., **US Patent 4,594,286**, Jun. 10, 1986.]

Raw material	Concentration, wt%
PVC	9.47
Blocked polyester polyurethane polymer	6.63
Chlorinated paraffin (40% Cl)	5.26
Chlorinated paraffin (70% Cl)	5.26
2-ethylhexyl diphenyl phosphate	8.42
Antimony trioxide	22.36
Zinc oxide	2.05
Decabromodiphenyl oxide	15.79
Zinc borate	15.79
Fume silica	0.63
Water repellent (zirconium wax complex)	0.5
Epoxidized soybean oil	0.05
Ba/Cd stabilizer (now obsolete)	0.3
Pigments	7.49

The substrate of the fabric is composed of untwisted, continuous multi-filament yarns such as polyester or polyamide that are free to flatten out in the fabric like miniature ribbons. These flat yarns have no more than the usual producers twist of one or two turns per inch. The flat yarns are woven into a fabric containing forty-four warp yarns per inch and thirty-two filling yarns per inch in a plain weave.

Synthetic leather top coat. [Data from Buess, P, Caers, R F, Colle, K S, Godwin, A, Saleh, R Y, Stanat, J E R, Less, D, **European Patent EP2268727**, Jan. 5, 2011, *ExxonMobil Chemical Patents Inc.*]

Raw material	Concentration, parts
PVC	100
Polyol ester plasticizer (this invention)	15
DINP	30
Calcium carbonate	5
TXIB	3
Stabilizer	3

4.24.3 CONVEYOR BELTS

4.24.3.1 Formulation found in the open literature

Conveyor belt as per Great Lakes recommendation. [Data from Coaker, A. W., *J. Vinyl Additive Technol.*, **9**, 3, 108-115, 2003.]

Raw material	Concentration, parts
PVC (E, K=70)	100
Reofos 50	40
DOP	20
Cereclor S.45	20
Antimony oxide	6
Zinc borate	4
Alumina trihydrate	10
Antistat (QAT)	4
Pigment	5
Antistat (PEGMO)	6
Stabilizer	2
Pigment	5

4.24.3.2 Patented inventions

Conveyor belt covering. [Data from Godwin, A D, Gosse C, **European Patent EP2358801**, Aug. 24, 2011, *ExxonMobil Chemical Patents, Inc*.]

Raw material	Concentration, parts
PVC dispersion resin	100
Di-C7 terephthalate	60-90
Filler ($CaCO_3$)	0.25
Antistats	5-10
Stabilizer	2-3

4.24.4 FLOORING

4.24.4.1 Formulation proposed by the raw material suppliers

Flooring. [Data from **Eastman TEG-EH**. Publication L-219A. *Eastman*, December 1997.]

Raw material	Concentration, parts
Lucovyl PB 1702 (dispersion resin)	80
Vinnol C65 (blending resin)	20
DOP	15
BBP	20
Eastman TEG-EH	15
Lankromark LZ 792	2.2
Lankromark ED6	3

Decor layer. [Data from Eichhloz, H, Martinz D O, **Solvin Paste PVC Handbook**. *Solvay*, 2010.]

Raw material	Concentration, parts
PVC	100
Plasticizer DINP	65
Mineral filler ($CaCO_3$ 15 μm)	15
Titanium dioxide	5
Activated blowing agent	3

Impregnation layer. [Data from Eichhloz, H, Martinz D O, **Solvin Paste PVC Handbook**. *Solvay*, 2010.]

Raw material	Concentration, parts
PVC	100
Plasticizer DINP	50
Plasticizer TXIB	10
Mineral filler ($CaCO_3$ 15 µm)	40
Stabilizer (CaZn)	2.5

Backing foam. [Data from Eichhloz, H, Martinz D O, **Solvin Paste PVC Handbook**. *Solvay*, 2010.]

Raw material	Concentration, parts
PVC	100
Plasticizer DINP	65
Mineral filler ($CaCO_3$ 15 µm)	40
Blowing agent (azodicarbonamide)	3
Kicker	2

4.24.4.2 Formulations found in the open literature

European flooring. [Data from Bohnert, T.; Izadi, R.; Pitman, S.; Stanhope, B., *J. Vinyl Additive Technol.*, **5**, 3, 143-147, 1999.]

Raw material	Top coat, parts	Foam, parts
PVC	100	100
Plasticizer(s)	44	40
Stabilizer	1.4 (Sn)	1.5 (Ba/Zn)
Epoxidized soybean oil	2.4	5
Carboxylic acid derivative		5
Glycol diisobutyrate		10
Calcium carbonate		30
Azodicarbonamide		3
Titanium dioxide		3

Flooring (different layers). [Data from Howick, C. J.; McCarthy, S. A., *J. Vinyl Additive Technol.*, **2**, 2, 134-142, 1996.]

Raw material	Concentration in different layers, parts			
	impregnation	print foam	wear	backing
Evipol MP7151	75			75
Evipol EP6779		80		
Evipol MP8058			75	
Vinnolit C65V	25	20	25	25
$CaCO_3$	75	25		75
TiO_2	10	10		
BBP	15	15	15	10
DOP	45			
DINP		40	40	40
Azodicarbonamide		3.5		
VD	1	1	1	1
Ba/Zn stabilizer	2	2		2
Sn stabilizer			1	
Epoxy stabilizer	3	3		3
White spirits	5	10		3

BBP – benzyl butyl phthalate; DOP – dioctyl phthalate, DINP – diisononyl phthalate; VD – viscosity depressant

4.24.4.3 Patented inventions

Fiberglass flooring system. [Data from Sultan, J., **US Patent 7,326,661**, Feb. 5, 2008.]

Figure 4.37 shows the cross-section of a flooring system. The yarns are conventionally woven into a fabric (17), which is bonded to a backing (19) to produce flooring (21). PVC backing has a thickness ranging between about 62.5 and 250 mills. The fabric has a thickness ranging between about 25 and 60 mills. Figure 4.38 shows a cross-section of fiber (11) which comprises a ceramic core (13) and a PVC jacket (15). Flooring can be produced in a tile form. It has very good cushioning, and it is durable and wipeable. The flooring is abrasion resistant, and it does not show color change during use.

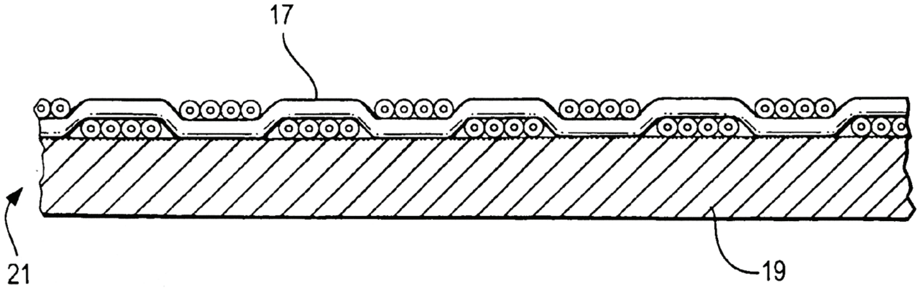

Figure 4.37. Cross-section of flooring system. [Adapted from Sultan, J., **US Patent 7,326,661**, Feb. 5, 2008.]

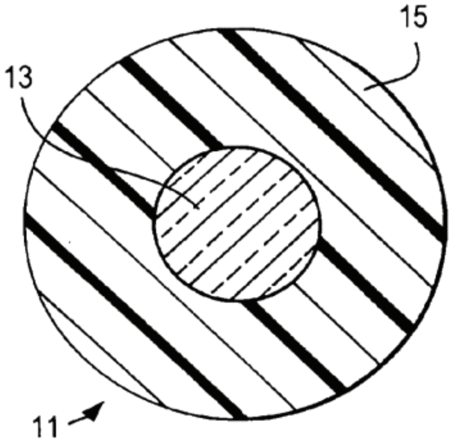

Figure 4.38. Cross-section of fiber. [Adapted from Sultan, J., **US Patent** 7,326,661, Feb. 5, 2008.]

Recycled synthetic flooring [Data from Junior, S., **WO2015028390A1**, *Tarkett Gdl S.A.*, Mar. 5, 2015.]

Raw material	Concentration, wt%
Dolomite	82.18
Recycled PVC	7.5
Epoxidized soybean oil	3.67
PVC S copolymer	2.5
Talc	2
Hydrocarbon resin (lubricant)	1.3
Pigment	0.85

Moisture-absorbing back-coating layer of decorative flooring system.

[Data from Anspach, K. M.; Kauffman, W. J., **US Patent 6,902,823**, Jun. 7, 2005.]

Raw material	Back coating	Lacquer
	Concentration, parts	
PVC dispersion resin	90	
PVC blending resin	10	
Primary phthalate plasticizer	30.6	
Secondary plasticizer	20	
Stabilizer	3	
Viscosity control agent	0.5	
Epoxidized soybean oil	2	
Antistat (HHTS 905 from BASF)	26.5	
Superabsorbent particles (Aqua Crystal, Na polyacrylate)	2.5	4.8
VC copolymer (VAGF from Union Carbide)		13.4
Methyl ethyl ketone		50
Methyl isobutyl ketone		12.5
Stabilizer (Thermolite T-31)		0.3
UV optical brightener (UVOB)		0.008
Polyether glycol (molecular weight=600)		19

The water permeable polymer matrix allows the water or moisture contained in the adhesive to migrate to the superabsorbent water retentive particles at a rate that will enable bonding to occur within a desirable time. The rate of bonding is dependent upon the type of adhesive used, the amount of water found in the adhesive, and the rate of moisture migration into the water retentive particles. The rate of drying of the adhesive is controlled, such that it does not dry too quickly, thereby resulting in a loss of adhesion, and allowing appropriate time for installation.

Lacquer was coated on the back of non-aqueous absorptive, vinyl-backed, commercially available sheet flooring. The application weight was about 13 g/sq. foot. The material was dried at 93°C for 1 hour. The back coating was coated on release paper. The application weight was about 8.5 g/sq. foot. The coating was gelled at 160°C for 5 minutes. Then the superabsorbent particle coated release paper was laminated to the back of previously coated non-aqueous absorptive flooring. A water-based adhesive layer was applied directly on the water absorptive back coating.

Resilient flooring. [Data from Hynicka, S. F.; Barshinger, D. E.; Schneider, D. E., **US Patent 6,818,282**, Nov. 16, 2004.]

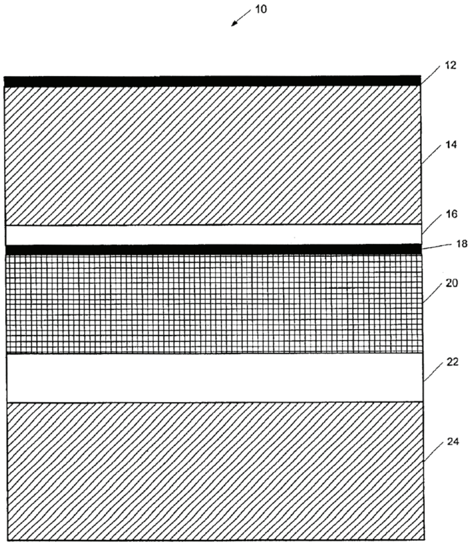

Figure 4.39. Cross-section of flooring system. [Adapted from Hynicka, S. F.; Barshinger, D. E.; Schneider, D. E., **US Patent 6,818,282**, Nov. 16, 2004.]

Figure 4.39 shows one structure developed according to this invention. A print on a scrim-resilient flooring structure (10) includes a base layer (24) having a thickness of about 40 mils, a first plastisol layer (22) having a thickness of about 10 mils, a scrim (20) having a thickness of about 10 mils, a second plastisol layer (16) (optional) having a thickness of about 5 mils, a hot melt calendered clear layer (14) having a thickness of about 15 mils, and a high performance coating (12).

The print on the scrim structure is formed by performing the following steps. A filled calendered base layer (24) is first prepared. A plastisol (22) is then applied by the rotary screen to the calendered base layer (24). The plastisol thickness depends on the scrim gauge. The scrim (20) is next introduced into the plastisol (22) using the nip of a rotary drum. The scrim (20) can include a woven glass mat or a non-woven mat. The gap between the drum and rubber roll is adjusted to prevent or minimize saturation of the plastisol to the scrim surface. The composite structure is then gelled around the heated drum. The desired pattern (18) is printed by rotogravure on the protruding surface of scrim (20). A second plastisol (16) is then applied by the rotary screen to the scrim (20). The plastisol coating, which can be applied by roll or blade, helps to tie the glass fibers of a woven glass mat scrim and acts as a critical coat for bonding of the hot melt calendered clear layer (14) to the glass mat scrim (20). This composite structure is then oven-fused. The calendered clear layer (14) is then applied to the composite structure. Finally, the high-performance coating (12) is applied using a well-known soft roll or air knife type coating processes.

The desired visual pattern (18) can be printed only on the surface of the scrim (20). If the scrim (20) is an open or weave type, the printed visual (18) is localized only on the scrim, thereby producing a discontinuous pattern that follows the detail of the scrim's construction. It is also possible to embed the scrim into the vinyl base layer (24) to produce a smooth surface that can be printed. In this instance, the print image is not confined to the scrim surface.

All layers with the exception of scrim fabric, high-performance coating, and print are made out of PVC plastisol or melt (as indicated in the text above). High-performance coating is either polyurethane, polyester, or UV curable.

Wear layer. [Data from Courtoy, J.-F.; Charest, C., **US Patent 6,586,108**, Jul. 1, 2003.]

Raw material	Concentration, parts
E-PVC (Oxy 75HC)	100
Tetraethylene glycol dimethylacrylate (SR 209)	55
Urethane acrylate and ethoxylated trimethylolpropane triacrylate=3:1 (U26253)	7.5
Heat stabilizer (BZ 512)	6
Photoinitiator (Irgacure 184)	1
Siloxane air release agent (BYK 3105)	0.5
Hindered phenol antioxidant (Irganox 1010)	0.05
Film thickness, mils	8
Tensile strength, psi	88
Elongation, %	25
Solvent resistance	excellent

Included in the table properties are achieved after thermal fusion at 200°C for 2 min and UV irradiation curing (5 sec under medium power mercury lamp of 150 W/sq. foot).

Non-stain flooring. [Data from Shortland, A. J.; Masters, K. A., **US Patent 6,579,610**, Jun. 17, 2003.]

Raw material	Concentration, parts
PVC	100
Plasticizer	30-70
Mineral filler	0-100
Thermal stabilizer	1-3
Pigment	1-6

Figure 4.40 shows a cross-section of flooring of this invention. A flooring material (1) comprises a base portion (2) having a coating portion (3) which imparts improved stain resistance to the flooring material (1) and is positioned in contact with an upper surface of the base portion (2). The coating portion (3) creates an upper surface of the flooring material (1). A particulate material (6) is embedded in the coating material (3) and at least partially penetrates the base por-

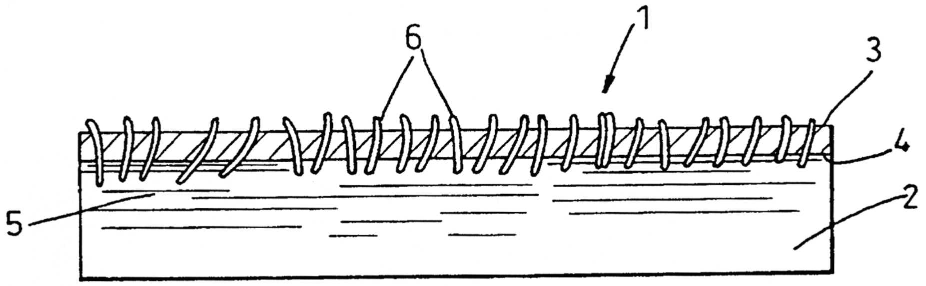

Figure 4.40. Non-stain flooring. [Adapted from Shortland, A. J.; Masters, K. A., **US Patent 6,579,610**, Jun. 17, 2003.]

tion (2). The particulate material (6) provides a roughened effect to the upper surface of the flooring material (1) and protects the coating from wear. The coating (3) merges into the base portion (2) where they meet at the joint (4) to form a stratified portion (5).

The powder is blended with the paste at an addition level of 1 wt%. The paste is spread coated at a thickness of 2 mm by knife over roller over the bed on to nonwoven support. Particles of silicon carbide and colored quartz are each scattered on the surface at the rate of 100 g/m^2. The paste is then gelled for 3 minutes at 170°C. Powder at the rate of 50 g/m^2 is applied, and further silicon carbide is applied at the rate of 100 g/m^2. The product is then fused at 190°C for 3 minutes and embossed.

The base portion is made of PVC and the coating portion is also made of PVC. Their formulations are given in the above table.

Flooring. [Data from Stevenson, D. R.; Harr, M. E.; Hood, B.; Jennings, T., *Plastics Additives Compounding*, **2**, 28-32, 2002.]

Raw material	Concentration, parts
PVC	100
Plasticizer	45
Epoxidized soybean oil	5
Calcium carbonate	20
Stearic acid	0.25
Alkyl bisphenol-A phosphite (Doverphos 675)	3.1
Tetraphenyl diphosphite (Doverphos 11)	0.75
Zinc octanoate	0.15

The phosphite esters function in this formulation as primary heat stabilizers by replacing labile chlorine atoms in PVC *via* the Arbuzov rearrangement mechanism. When phosphites are used at optimized levels in combination with catalytic amounts of zinc and normal levels of epoxidized soybean oil, they provide excellent early color and adequate long-term stability to flexible PVC compounds. Their use also helps in lowering stabilization cost, elimination of toxic metals, elimination of plateout, poor printability, viscosity drift in plastisols, haze, bloom, water blush, and staining.

Flooring sheet. [Data from Nakano, R., **US Patent 6,022,606**, Feb. 8, 2000.]

Raw material	Concentration, parts
PVC	100
Chopped short glass fibers	3
DOP	24
Epoxidized soybean oil	3
Ba/Zn stabilizer	2.5
Modifier	1.5

Wear layer. [Data from Shalov, A. A.; Placente, A. N., **US Patent 5,830,937**, Nov. 3, 1998.]

Raw material	Foam	Intermediate wearlayer	Wearlayer
	Concentration, parts		
PVC (Geon 180)	450		
PVC (Occidental 567)	250		
Plasticizer	350		
Alkyl & aryl hydrocarbons (Exxon Aromatic 150)	40	80	17
2% mildewcide in BBP	70		
Mineral spirits	3		
Blowing agent	30		
Filler	300		
PVC (Oxy 89HC)		550	
PVC (Borden 440)		300	433
PVC (Oxy BR501)		50	
Plasticizer (Eastman TXIB)		137	
Alkyl glycol benzoate (Occidental N6000)		162	
Alkyl benzyl phthalate (Monsanto S261)		180	
Heat/light stabilizers (Synpron 1559 & BYK 4015)		29	40
Epoxidized soybean oil		45	
DOA			87

Wear layer. [Data from Shalov, A. A.; Placente, A. N., **US Patent 5,830,937**, Nov. 3, 1998.]

Raw material	Foam	Intermediate wearlayer	Wearlayer
	Concentration, parts		
Aromatic and paraffinic hydrocarbons (Monsanto S375)			22
1,6-hexanediol monohydroxy			270
Dipentaerythritol monohydroxy penta acrylate (Sartomer 399)			120
Photoinitiator (Irgacure 500)			13
Coating thickness, mils	14	6	4

Curing the wear layer occurs in a UV oven which is nitrogen blanketed (200-600 ppm residual oxygen).

Crosslinked plastisol for surface layers. [Data from Kitazawa, K.; Ohrui, K.; Nakamura, E., **US Patent 5,444,110**, Aug. 22, 1995.]

Raw material	Concentration, parts
PVC	100
DOP	60
Octytin mercapto stabilizer	2
Phosphate	1
2,4,6-trimercapto-s-triazine	0.3
γ-aminopropyltriethoxysilane	1
Degree of crosslinking	7.4
Adhesion strength (cure 3 min at 190°C), kg/cm^2	1.4
Thermal stability (time to black at 200°C), min	20
Resistance to whitening (haze in % after 4 h in H_2O)	2.6

Floor and wall covering with barrier layer. [Data from Andersson, K. T., **US Patent 5,460,855**, Oct. 24, 1995.]

Raw material	Concentration, parts
PVC dispersion resin (Oxy 605, K=62)	64
S-PVC (Pliovic M 50, K=55)	36
Plasticizer (Monsanto S-377)	11
Diisononyl phthalate	11
Plasticizer (TXIB)	10

Floor and wall covering with barrier layer.

[Data from Andersson, K. T., **US Patent 5,460,855**, Oct. 24, 1995.]

Raw material	Concentration, parts
Organotin stabilizer (Stanclere T-4851)	3
Wetting agent (BYK-4010)	5
Sodium silicate solution (40% solids)	15

The back side of the substrate is coated with the above formulation to prevent migration of organic stains from the underlining floor or wall into the decorative portion of the covering material.

Flooring coated by reverse-roll-coater with monolithic particles.

[Data from Piacente, A. N.; Papp, G. J.; Whitehouse, R. E.; Mansolillo, R. D., **US Patent 5,178,912**, Jan. 12, 1993.]

Raw material	Foam	Wearlayer	Particles
	Concentration, parts		
PVC dispersion resin (Goodyear 180)	250		
Dispersion resin (Borden 432)	300		
S-PVC (Goodyear M70)	300		
PVC dispersion resin (Oxy 80HC)		400	
PVC dispersion resin (Oxy 1732)		450	
S-PVC (Oxy BR501)		150	
PVC (Vygen 310)			200
Diisobutyrate (TXIB)		150	9.3
Benzyl butyl phthalate	277	110	86
Alkyl benzyl phthalate		110	
Alkyl aryl hydrocarbon	150	30	
Ba/Zn stabilizer		30	
Tin stabilizer			5.2
Epoxidized soybean oil		50	17.6
2% Mildewcide in BBP	63		
Mineral spirits	15	35	
Azodicarbonamide	50		
Calcium carbonate	350		
UV stabilizer (benzophenone)		3	1
Titanium dioxide			31.2
Silica drying agent			3

Hybrid flooring. [Data from Kauffman, W. J.; Lilley, G. L.; Ruch, D. E., **US Patent 5,188,874**, Feb. 23, 1993.]

Raw material	Base	Foam	Clear	Back
	Concentration, parts			
PVC dispersion resin	66	66	30	60
PVC extender resin	34	34		40
PVC dispersion resin (higher molecular weight)			70	
Monomeric plasticizer	62	62	45	62
Azodicarbonamide	0.8	1.5		
Kicker	0.6	0.6		
Thermal stabilizer	0.7	0.7	1	1.5
Limestone filler	50	50		50
Viscosity diluent			5	
Pigment				3
Coating thickness, inch	0.021	0.006	0.01	0.012

The floor covering is a hybrid surface covering which is capable of accommodating the dimensional change of a target subfloor by utilizing the characteristics of both tension floorings and loose-lay floorings. Surface covering has a reinforcing layer which is an expandable diagonal pattern glass mat in which the glass mat is encapsulated with a plastisol. Because of the controlled pre-stressed condition of the reinforcing layer, the adjacent sides of the slits are pulled apart. The slits interact to form pivot points, which cooperate such that the reinforcing layer is capable of increasing and decreasing in dimension, respectively, in a direction generally transverse to the applied tensile or compression force. The substrate is coated on both sides by base and back layers, respectively. The base layer is coated with a foam layer, printed, and coated again with a clear, protective layer.

Birefringent flooring. [Data from Courtoy, J.-F.; Nedea, C., **US Patent 5,230,942**, Jul. 27, 1993.]

Raw material	Base	Transparent	Protective
	Concentration, parts		
PVC dispersion resin (K=67, Oxy 625)	70		
PVC dispersion resin (Oxy 68 HC)		97	
PVC extender resin (Oxy 567)	30	3	
Butyl benzyl phthalate	35	10	
DOP	8		
Texanol isobutyrate	12	10	
Phosphate ester (Reofos 50)		5.5	
Monoisobutyrate monobenzoate ester (Nuoplaz 1046)		32	
Titanium dioxide	5.5		
Calcium carbonate (Snowhite 9)	11		
Antimony trioxide	5.5		
Azodicarbonamide	3.4		
Zinc oxide	1		
Ba/Zn stabilizer (Synpron 1363)		3	
Mineral spirits	3		
Flitters (PS HR 422 from Mazzacca Corp.)		4	
Water-base polyurethane coating (Permuthane)			100
Antifoaming agent (BYK)			0.125

This invention relates to plastisol containing birefringent particles (flitters) dispersed in plastisol of a clear layer. The presence of flitters has decorative value in flooring compositions unless flitters are swelled by plasticizers. It is believed that the PVC particles and the flitters compete for the absorption of the liquid constituents of the plastisol and that ultimately, there is little absorption or no absorption at all of these liquid constituents by the flitters, thus preventing them from swelling. It is the swelling of the flitters that makes them lose their birefringence. This belief is supported by the fact that when the clear or translucent PVC plastisol is maintained at the fusion temperature (about 170°C) for a period of time longer than what is usually required, the color of the flitters tends to change slightly, but well after the PVC particles have darkened and decomposed. It is well known that in plasticized PVC, the plasticizer is not immobilized by the PVC, but rather that a balanced mobilization of the plasticizer is observed. This is illustrated by migration phenomena of plasticizers, which are very common and well-known.

Static dissipating flooring. [Data from Felter, R. E.; Markley, D. A.; Musser, D. L., **US Patent 5,066,422**, Nov. 19, 1991.]

Raw material	Black layer	White ink
	Concentration, parts	
PVC	100	100
DOP	30-60	28
Isobutyrate		11
Butyl benzyl phthalate	10	
Epoxidized soybean oil	5	5
Polyethylene glycol (PE 200)	1	
Organotin stabilizer (M-275)	2	2
Titanium dioxide	2	1.5
Isopropyl triisostearoyl titanate (KR55)	0.1-0.16	
Carbon black powder (Conductex 975)	0.6-4.8	

Conductivity depends on the proportions between the white ink and the black substrate.

Flooring with reduced electric resistivity. [Data from Dees, M.; Felter, R. E.; Musser, D. L., **US Patent 5,073,425**, Dec. 17, 1991.]

Raw material	Interlayer	Clear layer
	Concentration, parts	
PVC dispersion resin (Vestolit B7201)	80	
PVC extender resin (Vinnol C65V)	20	
PVC (Oxy 1734)		100
Quaternary ammonium antistat (Larostat 447)	7.2	1
Aluminum oxide trihydrate	90	
Stabilizer (dibutyltin maleate, M-275)	2	2
Plasticizer (ethylene oxide adipate, Bisoflex 124)	33	12
DOP	25	16
Epoxidized soybean oil	5	5
Flexibilizer (isobutyrate)	12	11

This flooring is composed of 3 layers: interlayer, a print layer, and a clear layer. The above table gives the formulation of plastisols used in the formation of the interlayer and the clear layer. The interlayer is coated on a glass scrim. This flooring was developed for use on floors, walls, and counter spaces in rooms where electronic components and circuit boards are manufactured and packaged. The low resistivity is required to prevent damage of electric components by static charges. Surface resistivity was 3×10^8 ohm/sq. at 50% RH and 2×10^9 ohm/sq. at 15% RH.

Flooring with reduced water absorption. [Data from Baker, P., **US Patent 4,925,883**, May 15, 1990.]

Raw material	Concentration, parts
PVC	55
VC/VAc copolymer	55
Titanium dioxide	10
Ester plasticizer	40
Hydrocarbon resin	10
Coarse ground limestone	660
Fine ground limestone	160
Ba/Zn stabilizer	2
Pentaerythritol	1.5
Melamine	1.5
Benzoic acid	0.5

4.24.5 SWIMMING POOL LINERS

4.24.5.1 Formulation found in the open literature

Swimming pool liner. [Data from Stevenson, D. R.; Harr, M. E.; Hood, B.; Jennings, T., *Plastics Additives Compounding*, **2**, 28-32, 2002.]

Raw material	Concentration, parts
PVC	100
C7-11 phthalate plasticizers	55
Epoxidized soybean oil	3
Titanium dioxide	7
Stearic acid	0.3
Phosbooster DP150 or DP160	3.5

4.24.5.2 Patented invention

Pool liner. [Data from Zelazny, J.; Morse, D. R., **US Patent 5,191,007**, Mar.2, 1993.]

Raw material	Invention	Comparative
	Concentration, parts	
Ultrahigh MW PVC (Oxy 410)	50	
High MW PVC (VC 106)	50	100
Epoxidized soybean oil	5	5
Ba/Zn stabilizer (Mark 4731)	2	2
Plasticizer (Jayflex 91, Jayflex 7911)	58	55
Biocide (Vinyzene BP5-5)	1.2	1
UV absorber (HHBP)	0.3	0.25
Acrylic process aid (Acryloid K120-N)	1.5	1
Stearic acid lubricant	0.4	0.4
Pigment	q.s.	q.s.
Tensile strength, psi MD/TD	3152/2762	2500/2200
Elongation, % MD/TD	463/524	350/380
Cold crack, ^{o}F	-40	-20
Compression set, %	39.5	44.5

4.24.6 TARPAULINS

4.24.6.1 Formulation proposed by the raw material supplier.

Adhesion layer. [Data from Eichhloz, H, Martinz D O, **Solvin Paste PVC Handbook**. *Solvay*, 2010.]

Raw material	Concentration, parts
PVC	100
Plasticizer DINP	80
Epoxidized soybean oil	4
Isocyanate adhesion agent	6
Stabilizer	2

4.24.6.2 Patented invention

Process of manufacture of tarpaulin or flooring. [Data from Plusquellec, P; Verhulst, J.; Perillon, J.-L., **US Patent 5,965,198**, Oct. 12, 1999.]

Raw material	A	B
	Concentration, parts	
Emulsion PVC (K=80)	45	80
Emulsion PVC (K=70)		20
Microsuspension PVC (K=70)	45	
Extender PVC (K=65)	10	
Benzyl butyl phthalate	40	
DOP	10	70
Ba/Zn stabilizer	5.7	2
Epoxidized soybean oil	5.7	
UV stabilizer	0.3	
Titanium dioxide		1
Calcium carbonate		60

Figure 4.41 shows a schematic diagram of the process line. A hopper (2) containing plastisol (3) is used in combination with a station for depositing (4), for example, a doctor blade, the plastisol (3) as a layer onto flat support (5), to obtain a coating layer (6) in the pasty state. The flat support (5) allows the coating layer in the pasty state to be supported on a release paper, a non-woven of inorganic fibers or a metallic or nonmetallic, nonadhesive endless belt.

Further downstream, there is a gelling station (7). Between the depositing station (4) and the station for gelling (7) the plastisol (3), there is a powdering station (8). This powdering station includes a source (9) of a plastic powder (10) including particles of thermoplastic material for incorporation and means for accelerating (11) the particles of the powder (10) toward the external surface of

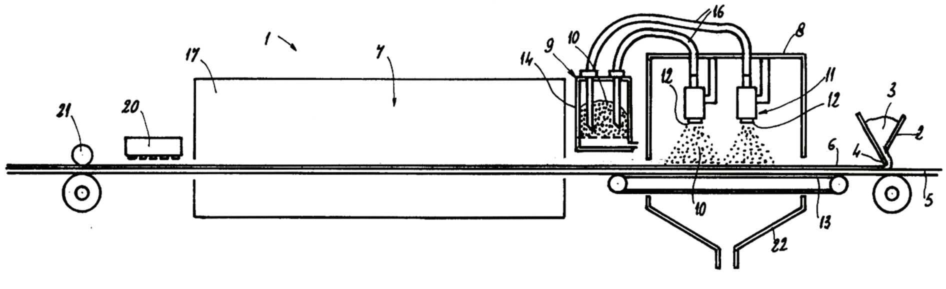

Figure 4.41. Schematic diagram of coating line. [Adapted from Plusquellec, P; Verhulst, J.; Perillon, J.-L., **US Patent 5,965,198**, Oct. 12, 1999.]

the coating layer (6) and for distributing the particles on the coating layer. The means for accelerating and distributing (11) are arranged and controlled to homogeneously incorporate the distributed and accelerated particles on a surface layer of the coating layer.

The means for accelerating (11) and distributing the plastic powder (10) for incorporation include hardware for spraying by an electrostatic route, with means for interposing the coating layer in the pasty state between a nozzle for ejecting (12) the plastic powder (10) and the support (13) of a metallic target. This support (13) is, for example, a metallic conveyor belt which is grounded. The source (9) of plastic powder (10) for incorporation may consist of a storage tank (14) connected to the ejection nozzles (12) by feed conduits (16) for the plastic powder and a feed entry (15) for the recovered particles. They are preferably PVC particles. The composition of plastisol is given in the above table.

4.24.7 UPHOLSTERY

4.24.7.1 Formulation found in the open literature

Crosslinked foamed layer. [Data from Yanez-Flores, I. G.; Ibarra-Gomez, R.; Rodriguez-Fernandez, O. S.; Gilbert, M., *Eur. Polym. J.*, **36**, 10, 2235-2241, 2000.]

Raw material	Concentration, parts
PVC (K=66)	100
DOP	80
Azodicarbonamide	2
Ca/Zn stabilizer	4
Kicker	4
Peroxide	2
Trimethylolpropane-trimethylacrylate, TMPTMA	15

The peroxide/TMPTMA system permits the formation of a dense network, because of the trifunctional character of the coagent. There is no residual unsaturation. The thermal stability of the sample is better than the commercial foam.

4.24.7.2 Patented inventions

PVC flame retardant compositions [Data from Zucchelli, U, **US20150353711A1**, *Italmatch Chemicals SpA*, Dec. 10, 2015.]

Raw material	Concentration, parts
PVC K=70	100
Santicizer 2148	50
Stabilizer (Repak G-NT/7526)	3
Costabilizer (Reaflex EP/6)	5
Sb_2O_3	3

4.23.8 WALLCOVERING

4.23.8.1 Formulations found in the open literature

Wallcovering. [Data from Howick, C. J.; McCarthy, S. A., *J. Vinyl Additive Technol.*, **2**, 2, 134-142, 1996.]

Raw material	Concentration, parts
PVC	100
Diisobutyl phthalate	50
Chlorinated paraffin	20
Plasticizer/diluent	10
Stabilizer	1
Pigment	quantum satis
Calcium carbonate	62.5
White spirits	10

This formulation was used as a worse-case scenario formulation to predict indoor emissions from PVC products. It can be representative of some low-cost formulations, but it is not suggested as a base formulation for production.

Wallcovering. [Data from Stevenson, D. R.; Harr, M. E.; Hood, B.; Jennings, T., *Plastics Additives Compounding*, **2**, 28-32, 2002.]

Raw material	Concentration, parts
PVC	100
DOP	25
Calcium carbonate	25
Epoxidized soybean oil	3
Titanium dioxide	7
Stearic acid	0.5
PhosBooster DP410	4

This formulation is stabilized with non-metal containing stabilizers (phosphite and epoxy). Studies show that performance is equivalent to material stabilized with Ba/Cd or Ba/Cd/Zn stabilizers.

4.24.8.2 Formulation proposed by the raw material supplier

Wall covering. [Data from Eichhloz, H, Martinz D O, **Solvin Paste PVC Handbook**. *Solvay*, 2010.]

Raw material	Concentration, parts
PVC	100
Plasticizer DINP	45
Viscosity depressant	5
Calcium carbonate	20
Titanium dioxide	5
Foaming agent (ADCM)	4
Kicker	1

4.24.8.3 Patented inventions

Wallpaper foam. [Data from Becker, H G, Grass, M, Huber, A, **European Patent EP2643399**, Oct. 2, 2013, *Evonik Oxeno GmbH*.]

Raw material	Concentration, parts
Vestolit E 7012 S	100
Hexamol DINCH	54
Uniform AZ ultra 1035	5
Microdol A1	20
Kronos 2220	8
Baerostab KK 48	2
Isopar J	3.5
Water	1

Wallcovering having low VOC. [Data from Sobieski, R. T.; Gottschalk, D. C., **US Patent 7,029,759**, Apr. 18, 2006.]

Raw material	Concentration, parts
PVC	100
Acrylic resin	2.5
Calcium carbonate	47
Aluminum hydrate	3
Ca/Zn stearate	0.25
Stearic acid	0.3
Zinc stearate	0.2

Wallcovering having low VOC. [Data from Sobieski, R. T.; Gottschalk, D. C., **US Patent 7,029,759**, Apr. 18, 2006.]

Raw material	Concentration, parts
Diisononyl phthalate	40.5
Anitfungal, antimicrobial compound	0.75
Epoxidized soybean oil	3
Organic phosphite containing diluent (alcohol having 12 or more carbon atoms)	2.2
Antimony oxide	4

Wallpaper. [Data from Stevenson, D. R.; Harr, M. E.; Jakupca, M. R., **US Patent 6,824,711**, Nov. 30, 2004.]

Raw material	Concentration, parts
PVC	100
Plasticizer	45
Epoxidized soybean oil	5
Calcium carbonate	20
Stearic acid	0.25
Alkyl bisphenol-A phosphite (Doverphos 675)	3.1
Tetraphenyl diphosphite (Doverphos 11)	0.75
Zinc octanoate	0.15

Wallpaper. [Data from Buess, P, Caers, R F, Colle, K S, Godwin, A, Saleh, R Y, Stanat, J E R, Less, D, **European Patent EP2268727**, Jan. 5, 2011, *ExxonMobil Chemical Patents Inc.*]

Raw material	Concentration, parts
PVC	100
Polyolester plasticizer (this invention)	10
DINP	35
Filler	10
Stabilizer	2.3
Lubricant	0.25

Wallpaper with matte finish. [Data from Iijima, S.; Yamamoto, T., **US Patent**, **5,770,641**, Jun. 23, 1998.]

Raw material	Concentration, parts
PVC (polymerized according to invention)	100
DOP	65
Calcium carbonate	50
Titanium dioxide	15
Azodicarbonamide	3
Thermal stabilizer	3
Diluent	5

The patent describes a method of production of PVC which gives low surface gloss, dry feeling, and appearance required in production of wallpaper, flooring, and other plastisol-based articles.

Self-adhesive wallcovering. [Data from Brown, K. D.; Williams, D. A., **US Patent** 5,413,829, May 9, 1995.]

Raw material	Concentration, parts
PVC	100
DOP	67
Filler	50
Titanium dioxide	35
Stabilizer	2
Coating weight, g/m^2	110

4.24.9 OTHER PRODUCTS

4.24.9.1 Patented inventions

Color sheet with light reflecting properties. [Data from Harasawa, J.; Suzuki, T.; Ashizawa, H., **US Patent 7,137,713**, Nov. 21, 2006.]

Raw material	Reflecting layer	Color layer
	Concentration, parts	
PVC (PX-QHPN from Shin Daichi)	100	
PVC (PSH-23 from Kaneka Co.)		100
Isononyl phthalate	70	70

Color sheet with light reflecting properties. [Data from Harasawa, J.; Suzuki, T.; Ashizawa, H., **US Patent 7,137,713**, Nov. 21, 2006.]

Raw material	Reflecting layer	Color layer
	Concentration, parts	
Glass balloons (Celstar Z27 from Asahi Glass Co.)	15	
Titanium dioxide	15	
Green pigment (KT-1800 from Tokushu Shikiryo)		1
Stabilizer (AC183 from Asahi Denka)	3	1
Thickness, mm	0.4	0.1
Solar radiation reflectance, %	83	46
Back surface temperature, °C	43	

Two layers were used in this example (more layers can be used as discussed in the invention). The bottom reflecting layer's properties determine the performance of the laminate regarding back surface temperature and solar radiation reflectance. Also, the ratio of the thicknesses of both layers affects properties.

Self-adhesive reinforced foam gasket. [Data from Sylvester, M. S., **US Patent 6,551,425**, Apr. 22, 2003.]

Raw material	Concentration, parts
PVC dispersion resin (Kaneka EH219)	34
PVC blending resin (Kaneka PBM B5F)	8
Phthalate plasticizer	34
Chlorinated paraffin	5
Calcium carbonate	14
Azodicarbonamide	4
Cell stabilizer (VS103 from Air Products)	0.5
Thermal stabilizer (5573 from Ferro)	0.5
Epoxidized soybean oil	0.5
Foam density, lb/ft^3	6-8

Figure 4.42 shows a cross-section of a PVC foam gasket. The gasket (30) comprises a release liner (40) comprising release paper (42) having a release (preferably silicone) coating (38) which provides a release surface. This release liner (40) has an upper surface which is a release surface. The release paper is about 78 lb., clay-coated, long-fiber, super-calendered, flat, heat-resistant paper. The plastic or polymeric film may be substituted for the paper layer (42). A layer of pressure sensitive adhesive (36) is applied to the release surface of the silicone

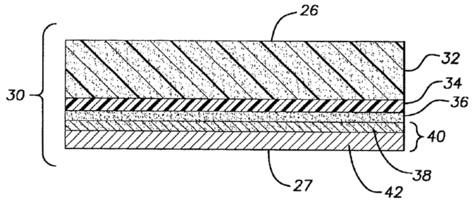

Figure 4.42. Cross-section of a gasket. [Adapted from Sylvester, M. S., **US Patent 6,551,425**, Apr. 22, 2003.]

release coating (38). The pressure sensitive adhesive layer (36) is a high-temperature rubber-based hot melt pressure-sensitive adhesive. Next, a layer of flexible polymeric film (34), polyester film, is applied to the layer (36). The flexible polymeric film layer (34) is about 1 mil thick polyester film, such as Mylar brand polyester film from DuPont. The flexible polymeric film layer (34) reinforces the gasket and prevents migration of plasticizer from the resilient foam layer (32) to the pressure-sensitive adhesive layer (36), where it would adversely affect and degrade the PSA. Flexible foam (32) is closed cell PVC flexible foam. After curing and solidifying, the flexible foam layer (32) is 3/16 to 1/4 inch thick.

Plasticizer from renewable resources. [Data from Wesch, K.; **US Patent 6,559,213**, May 6, 2003.]

Raw material	A	B	C	D
	Concentration, parts			
PVC dispersion resin (K=72)	17	17	17	17
PVC suspension resin (K=65)	4	4	4	4
Diisononyl phthalate	37	34	30	25
Rapeseed oil methyl ester	3	6	10	15
Petroleum 190/250	3	3	3	3
Ground chalk	12.37	12.37	12.37	12.37
Calcium oxide	1.5	1.5	1.5	1.5
Zinc oxide	0.2	0.2	0.2	0.2
Carbon black paste	0.03	0.03	0.03	0.03
Stearate coated precipitated calcium carbonate	13.6	13.6	13.6	13.6
Precipitated calcium carbonate	5	5	5	5
Fume silica	0.5	0.5	0.5	0.5
Polyaminoamide	0.8	0.8	0.8	0.8
Viscosity, Pas	1.38	0.97	0.83	0.65
Yield point, Pas	210	172	153	142
Shore A hardness	44	43	44	45
Tensile strength, N/mm^2	1.87	1.99	1.96	2
Elongation at break, %	195	190	176	162

Light shoe soles. [Data from Peretti, G.; Pasetto, R., **US Patent 6,184,259**, Feb. 6., 2001.]

Raw material	Concentration, parts
PVC	100
DOP	45
Diisobutyl phthalate	15
Epoxidized soybean oil	5
Ba/Zn stabilizer	5.5
Stearic acid	1
Polymeric microspheres containing isopentane	6

Addition of microspheres lowers the density of the resultant material to be in the range of 0.4 to 0.5 g/cm^3.

Foamed tape. [Data from Hilston, M. D.; Collins-Swavey, R.; Wanska, R.; Spilizewski, K; Carte, T.; Katona, R., **US Patent 6,077,986,** Jun. 20, 2000.]

Raw material	Concentration, parts
PVC dispersion resin	60
PVC blending resin	40
Polyester plasticizer	120
Activator/stabilizer	3
Azodicarbonamide	1.2
Defoamer	0.25
Odorless mineral spirits solvent	6
Flesh colored pigments	1.1
Foam density, lbs/ft^3	33
Elongation, %	272

Figure 4.43 shows a cross-section of foam tape. The liner backing (51) carries the release layer (52), onto which the adhesive (53) is disposed of. A barrier film layer (54) is disposed on the dried adhesive, over which plastisol (55) is coated. If the plastisol (55) is to be used as a skin bandage, it is rendered more permeable to air by perforation, such as by passing the foam or film carrying laminate in contact with a roller carrying pins for perforating the foam or film. The tape product is to be used as a bandage or wound dressing. The foamed PVC layer formulation is given in the above table.

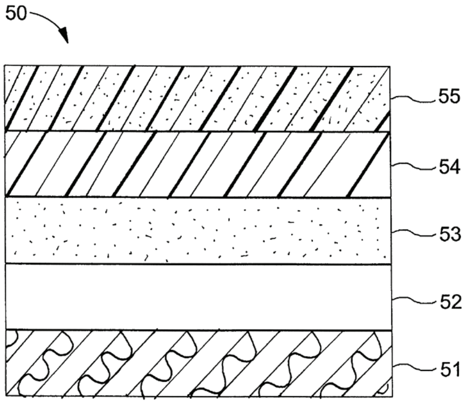

Figure 4.43. Cross-section of foam tape.
[Adapted from Hilston, M. D.; Collins-Swavey, R.; Wanska, R.; Spilizewski, K; Carte, T.; Katona, R., **US Patent 6,077,986**, Jun. 20, 2000.]

Radiation-attenuating sheet material for x-ray protective garment.

[Data from Lagace, A., **US Patent 6,153,666**, Nov. 28, 2000.]

Raw material	Concentration, parts
Metallic tin powder (AcuPowder 5325)	127.5
Barium carbonate powder	127.5
PVC dispersion resin (Geon 120)	20
Plasticizer (TEG)	18
Dispersing agent (BYK 1142)	2

It was found that 78 grams of the 4.5 inch squares were required to achieve the same attenuation, at 90 Kvp, as a lead foil 0.5 mm thick. When PVC matrix attenuation products are formed utilizing 100% lead powder, a standard weight of 85.5 grams of such squares is required. Thus, the same attenuation effectiveness was provided with a weight savings of 8.8%, utilizing the barium carbonate/tin containing matrix. For an unknown and unexpected reason, this was 7% lighter in weight than theoretical projections would expect.

Noise-damping coating. [Data from Wesch, K.; Ruch, K., **US Patent 5,756,555**, May 26, 1998.]

Raw material	Concentration, parts
VC/VAc copolymer (K=60)	45
Diisononyl phthalate	26
Calcium oxide	1
Chalk (ground)	15.5
Chalk (precipitated)	8
Zinc oxide	0.5
Polyaminoamide (Euretek 507 from Witco)	1
Naphtha (Isopar H from Exxon)	3

It is sprayable plastisol which can be used for coating substrates which require noise-damping, especially of high-frequency components.

Foamed tape. [Data from Cascino, L. A., **US Patent 4,981,755**, Jan. 1, 1991.]

Raw material	Concentration, parts
PVC	100
Plasticizer (glutarate ester)	100
Plasticizer (trimellitate ester)	10
Cell stabilizer	1
Thermal stabilizer	1.5
Kicker	1.5
Blowing agent	3.5
Viscosity depressant	10

Light-weight tenting fabric. [Data from McKinney, J. M.; Russell, J. S.; Samson, R. D., **US Patent 4,758,465**, Jul. 19, 1988.]

Raw material	Base coat	Top coat
	Concentration, wt%	
PVC		21.56
Water repellent (zirconium wax complex)		0.29
Antiblocking agent (Acrowax C)		1.17
Flame retardant (decabromodiphenyl oxide)	25	11.71
DOP	7.13	20.26
Pigment system (infrared properties, and green/white color)	7.13	7.13
Thermal stabilizer		0.64
Fume silica		1.29
Epoxidized soybean oil		0.64
Flame retardant (chlorinated paraffin 40% chlorine)		5.5
Flame retardant (chlorinated paraffin 70% chlorine)		2.43
Flame retardant (antimony oxide)	25	23.16
Inhibitor (zinc oxide)		2.14
Binder (polyester urethane)	25	

Antistatic composition. [Data from Geissel, F. A.; William W. A.; Rys-Sikora, J., **US Patent 4,594,367**, Jun. 10, 1986.]

Raw material	Concentration, parts
PVC	100
Fire retardant (hydrated aluminum oxide, Hydral 710B)	5
Plasticizer (diisoheptyl, Jayflex 77)	77
Plasticizer (DOP)	8.5
Epoxidized soybean oil	12
Tin stabilizer	2
Titanate (KR-55)	0.05
Zinc stearate	0.1
Stearic acid	0.5
Titanium dioxide	2.2
Carboxylated nitrile rubber (Krynac 221)	30
Non-ionic antistatic (Markstat AL-15)	5
Whitening agent (ultramarine blue)	0.005
Surface resistivity, ohms/inch^2	2.68×10^9

Base coating for non-woven substrates. [Data from Dost, G.; Gerber, W.; Jaeger, E.; Mueschter, E.; Weiss, R., **US Patent 4,464,432**, Aug. 7, 1984.]

Raw material	Concentration, parts
E-PVC (K=70)	150
Diisodecyl phthalate	140
Epoxidized soybean oil	6
Thermal stabilizer	9
Antiaging agent (hydroxybenzol)	1
UV absorber (benzotriazole)	0.5

The basecoat impregnates the substrate, making it useful for further processing, for example by lamination with another PVC layer to form a final product.

4.24.10 CONCLUSIVE REMARKS

Many different products are manufactured by coating, but all require plastisol which determines the need for certain major ingredients of formulation. The major components of the formulation include:

- PVC (all types of polymer (emulsion, suspension, microsuspension, and mass) are used in blending which helps to modify rheological properties of plastisols; molecular weight varies widely from low to ultrahigh)
- plasticizers (affect viscosity and non-Newtonian properties of plastisols, which emphasizes the importance of their selection; a large number of plasticizers are used, including most phthalates, with special interest in diisononyl phthalate, benzyl butyl phthalate, mixed alcohols (most frequently C7-C11 phthalates), di-(2-ethylhexyl) phthalate, DINCH but also benzoates (isononyl, 2-ethylhexyl, 2,5,5-trimethylhexyl), TXIB, DOA, chloroparaffins, phosphates (mainly tricresyl and 2-ethyl diphenyl) are used. Some less known, more recent plasticizers include N-dodecyl-2-pyrrolidone, an ester of diethylene glycol and a mixture of benzoic and lauric acids, and rapeseed oil methyl ester)
- thermal stabilizers are less critical than in other processing methods but not unimportant. A major group includes metal carboxylates (Ca/Zn and Ba/Zn), but tin stabilizers with or without sulfur are sometimes used as well; sodium perchlorate, epoxidized oils, and phosphites are secondary stabilizers in frequent use)

The above three components are sufficient to make suitable plastisols, but there are many special needs which require various other additives, such as:

- fillers (chalk, limestone, precipitates, surface coated calcium carbonate, short glass fibers, glass microspheres, and hollow thermoplastic microspheres),

- blending polymers (epoxy resin, polyurethane, acrylic, melamine, and carboxylated nitrile rubber),
- wetting and dispersing agents,
- flitters,
- diluents (white spirits, alkyl & aryl hydrocarbons, petroleum, & naphtha),
- viscosity regulators (fumed silica increases viscosity and thixotropic properties, and various viscosity depressants are used to lower viscosity),
- adhesion promoters (silane, urethane, polyadipic anhydride, and maleic anhydride),
- flame retardants (antimony oxide, zinc borate, aluminum hydroxide, decabromodiphenyl oxide, and mentioned above phosphate plasticizers and chloroparaffins),
- blowing agents (most frequently azodicarbonamide),
- kickers (or catalysts of decomposition of blowing agent),
- cell stabilizers,
- air release and antifoaming agents
- antistatics,
- UV stabilizers (titanium dioxide, carbon black, and antioxidants),
- optical brighteners and ultramarine blue,
- water repellents,
- photoinitiators,
- flexibilizers,
- mildewcides and biocides,
- antiblocking agents,
- stearic acid,
- acrylic process aid.

The most important properties of PVC plastisols are:

- viscosity (most frequently, low viscosity is important for the processing and reduction of a quantity of liquid additives; in fabric coating, medium to high viscosity is required to reduce penetration of plastisol into the fabric),
- rheological characteristic (pseudoplastic properties (low viscosity at high shear rate increases the coating rate and improves the surface of the coated layer, and increased viscosity at low shear rate that reduces penetration of plastisol into the supporting material (textile, paper, non-woven) are the most desirable in many applications, but other rheological characteristics are also useful),
- fusion rate,
- adhesion to the substrate and limited adhesion to release paper,
- mechanical performance.

Troubleshooting of foamed layers has been discussed in Section 4.8. Other formulation related problems include:

- poor control of coating thickness (plastisol has dilatant properties),
- air entrapment (plastisol has dilatant properties),
- plastisol aging (too high concentration of highly solvating plasticizers),
- long fusion time (too low concentration of highly solvating plasticizers),
- streaks (non-solvated particles, lumps, contamination),
- ribbing and cascading (ribbing consists of small raised sections in the coating material across the width of the rollers in the gap area; coating pulls from a metering roll as it leaves the metering nip and moves along with applicator roll. If this occurs in the center of the nip, the coating is smooth. If it occurs at the outlet side, ribbing occurs. If it occurs on the inlet side, cascading occurs. These defects are likely to be caused by too high surface tension and/or too low viscosity),
- chatter (a series of transverse marks or lines on a coated web; dilatant characteristic of plastisol causes instability),
- dripping or surface defects (rheological behavior of coating to be adjusted),
- edge beads (they are formed at the edges of the coating knife or roll and transferred to the material. Because they are thicker than the coating, they require a longer time to fusion, and if not fused properly, they wind onto the roll or stick to the paper web, causing it to tear off in extreme cases. The usual cause is too low viscosity, which means that rheological properties have to be adjusted to prevent sidewise flow of plastisol),
- craters (insufficient deaeration, too high surface tension),
- blisters (evaporation of volatiles),
- insufficient adhesion (adhesion promoter type or concentration),
- poor mechanical performance (insufficient fusion which requires modification of plasticizer selection or process conditions; general problems with formulation),
- color change (low thermal stability).

Further reading: Gutoff, Edgar B.; Cohen, Edward D.; Kheboian, Gerald I., **Coating and Drying Defects: Troubleshooting Operating Problems**, 2nd Edition, *Wiley-Interscience*, New York, 2006.

Wypych, G., **Polymer Modified Textile Materials**, *John Wiley & Sons*, New York, 1988.

4.25 WIRE & CABLE

4.25.1 FORMULATIONS PROPOSED BY THE RAW MATERIAL SUPPLIERS

Cable insulation (replacement of lead stabilizer). [Data from **Mark 6736ACM and Mark 6750ACM**. *Crompton*.]

Raw material	THHN/THWN	NM-B jacket
	Concentration, parts	
PVC (medium molecular weight)	100	100
Jayflex TINTM	25	
Jayflex UDP	25	
DIDP		55
Drapex 6.8		5
Calcinated clay	12	
Calcium carbonate		50
Antimony trioxide	2	
Mark 6736ACM (Ba/Zn carboxylate)	5	
Mark 6750ACM		5

Cable coating. [Data from **PVC recipes**. *Baerlocher*.]

Raw material	Maximum service temperature, ^oC			
	70	80	90	105-125
	Concentration, parts			
PVC (K=70)	100	100	100	100
Plasticizer	52 (DEHP)	55 (DIDP)	55 (DIDP)	50 (TOTM)
Filler	70-80	60-80	60-80	15-20
Ca/Zn stabilizer	3-3.5	4-5.5	4-5.5	8-12
Stabilizer type (Baerlocher)	KA 81/5	8703 KA/5	8823 KA	8553 KA-ST/3

Flexible PVC for cables. [Data from **Sorbacid 911. Hydrotalcite as costabilizer for PVC**. *Sued-Chemie AG.*]

Raw material	Concentration, parts
PVC (K=70)	100
Plasticizer	50
Filler	50
Ca/Zn stabilizer	1
Sorbacid 911 (hydrotalcite)	3

4.25.2 PATENTED INVENTIONS

Wire jacket for plenum cables. [Data from Abu-Ali, A F, Szylakowski, G R, Albrinck, A C, **European Patent EP2534201**, Dec. 19, 2012, *General Cable Technologies Corporation.*]

Raw material	Concentration, wt%
PVC resin	42.83
Brominated phthalate	5.57
Di-(2-propyl heptyl) phthalate	14.13
Chlorinate paraffin	6
Calcium-zinc stabilizer	3
Aluminum trihydrate	8.57
Antimony trioxide	1.71
Zinc borate	1.28
Stearic acid	0.09
Calcium carbonate	14.99
Silicon dioxide	1.84

Wire & cable coating. [Data from Watanabe, K.; Ito, H.; Saito, M.; Hayashi, T.; Hirayama, N.; Kobayashi, S.; Wakayama, Y., **US Patent 7,420,118,** Sep. 2, 2008.]

Raw material	**A**	**B**	**C**	**D**
	Concentration, parts			
PVC	100	100		100
Nitrile rubber	100			
EVA		100		
Chlorinated polyethylene-vinyl chloride grafted			100	
Ditridecyl phthalate (molecular weight=547)				80
Calcium stearate	4	2	5	2
Zinc stearate		2	5	2
Hydrotalcite	6	6		6
Calcinated clay	10	10	10	10
Antimony trioxide	6	6	6	6
Tetrakis-[methylene-3-(3',5'-diisobutyl-4'-hydroxy-phenylpropionate)methane]	0.3	0.3	0.3	0.3
Generated gaseous substance, μg/g	500	600	400	1700

In recent years, along with the high integration of semiconductor or liquid crystal device manufacturing apparatus, contamination of a substrate, in particular, of a silicon wafer due to absorption of molecular contaminant (Airborne Molecular Contaminants: AMCs) and adhesion of dirt has become a matter of concern. As a source of generating the AMCs, in addition to interior material of a clean room, electric wires or cables used in the clean room facility or during manufacturing various types of semiconductors, have been pointed out.

Plasticizers, which are widely used in electric wires or cables in PVC coatings, act as a main source of the AMCs. AMCs can be dramatically decreased by replacing plasticizers with high molecular weight and low vapor pressure additives.

Stabilizer change involves replacing traditional lead stabilizers with stabilizers which are substantially less toxic.

The above table shows that if the monomeric plasticizer (even having a very high molecular weight) is used (formulation D), it generates high emission of gaseous substances. But these emissions can be substantially reduced if blending is used instead of plasticization by classical plasticizers, as can be seen from formulations A-C.

Wire and cable coating compound (plasticizer replacement). [Data from Goss, C.; Larson, M.; Legrand, P. J. P.; Caers, R. F.; Daniels, P. H.; Godwin, A. D.; Naert, D., **US Patent 7,413,813**, Aug. 19, 2008.]

Raw material	Concentration, parts
PVC (Solvic 271 GC)	100
Di-(2-ethylhexyl) cyclohexanoic acid ester	50
Calcium carbonate (EXH1SP form Omya)	80
Tribasic lead stearate (Interstab PTS-E)	6
Dibasic lead stearate (Interstab P51)	1

Use of esters of cyclohexanone polycarboxylic acids, such as di(2-ethylhexyl) cyclohexanoic acid ester, enables one to produce materials having comparable mechanical properties with less PVC. It also increases UV stability, improves low-temperature properties, and reduces smoke on burning. Highly flexible and semi-rigid goods can be produced with these plasticizers.

Power transmission cable. [Data from Belli, S.; Bareggi, A.; Scelza, C., **US Patent 7,105,749**, Sep. 12, 2006.]

Raw material	Internal	External
	Concentration, parts	
PVC (K=70, Evipol SH7020)	100	100
Antimony trioxide	0.75	3
Calcium carbonate	60	100
Bisphenol A	0.62	0.2
Thermal stabilizer (dibutyltin dilaurate)	4	8
Plasticizer	38	40
Mineral charge	2.5	
Chlorinated paraffin		18
Flexural modulus, MPa	144	32.7
Ultimate tensile strength, MPa	16.8	14
Elongation, %	250	320

The invention relates to an electrical cable with increased flexibility, peeling-off properties, and increased intelligibility of the marked indicia. The electrical cable is designed for power transmission at low voltage, suitable for building wiring.

Cable. [Data from Scheidecker, R.; Reinhard, H.; Schwirblies, P.; Armstrong, H.; Aitken, H., **US Patent 7,132,604**, Nov. 7, 2006.]

Raw material	1st coat	2nd coat
	Concentration, parts	
PVC (K=70)	37.4	49.4
Plasticizer	20.5	24.6
Chalk	41.1	24.6
Stabilizer	1	1.2
Pigment		0.2

The object of the invention is to provide a cable, and a corresponding method of production with reduced weight and a reduced amount of extruded material for the outer sheath. The above table shows formulations which have been used by the inventors. It is also possible to use additives which cause expansion of the PVC layer and thus further reduce the weight of the layer.

The cable of the invention is used as a house wiring cable, which is installed in buildings for illumination purposes and power supply to electrical devices. Such cables are used in significant volumes all over the world. The advantages of the invention are low weight and the amount of sheathing material but also the reduced formation of smoke and release of heat. If it is required, flame retardants can be additionally added as a further improvement.

PVC composition containing PTFE powder. [Data from Lee, B.-L.; Patel, R.; Cox, M.; Andries, J., **World Patent WO/2005/000960**, Jan. 6, 2005.]

Raw material	Control	PTFE powder
	Concentration, parts	
PVC	100	100
Plasticizer	30	30
Lead stabilizer	6	6
Stearic acid	0.25	0.25
Barium stearate	5	5
Process aid	6	6
Fire retardant plasticizer A (not disclosed)	10	10
Fire retardant plasticizer B (not disclosed)	5	5
PTFE micropowder (e.g., Zonyl MP 1000, or Polymist F5A)	0	50

PVC composition containing PTFE powder. [Data from Lee, B.-L.; Patel, R.; Cox, M.; Andries, J., **World Patent WO/2005/000960**, Jan. 6, 2005.]

Raw material	Control	PTFE powder
	Concentration, parts	
Tensile strength, psi	4700	3100
Elongation, %	270	220
Peak heat release rate, kW/m^2	503	93
Char, %	15	10
Combustion heat, kJ/g	916	659

Addition of PTFE powder improves all parameters characterizing burning behavior of PVC cable compound.

Flame-retarded composition. [Data from Shah, M.; Fisch, M. H.; Stewen, U.; Bacaloglu, R., **US Patent 6,756,431**, Jan. 29, 2004.]

Raw material	Concentration, parts
PVC (Geon 30)	100
Plasticizer (trisnonyl trimellitate)	45
Brominated ester	20
Phosphate ester	10
ATH	70
Ba/Ca/Zn stabilizer	8
Fire retardant of invention (details in patent)	18
Antimony trioxide	3
Zn borate	5
Limiting oxygen index, %	38.4
Time to ignition, s	37
Peak heat release rate, kW/m^2	142
Total heat release, MJ/m^2	40.7
Average heat of combustion, MJ/kg	10.3
Total smoke release	1041

Flexible, flame-retarded composition. [Data from Day, J. F.; Good, J. J., **US Patent 6,534,575**, Mar. 18, 2003.]

Raw material	Control	Invention
	Concentration, parts	
PVC (Geon 30)	100	100
Antimony trioxide	15	15
Trioctyl trimellitate (Uniplex 546-A)	34.3	34.3
Lead stabilizer	5	5
Dioctyl tetrabromophthalate (Uniplex FRP-45)	40	30
Dioctyl tetrachlorophthalate (Uniplex FRP-27)	0	10
Tensile modulus at 100% strain, psi	1760	1963
Tensile strength at break, psi	2050	3391
Elongation, %	278	370
Limiting oxygen index, %	33	37
NBS smoke	440	276
Brittleness temperature, °C	-14	-25

Lead-free composition for thin-walled automotive cables. [Data from Delgado, A. H., **US Patent 6,642,293**, Nov. 4, 2003.]

Raw material	Concentration, parts
PVC (K-70)	100
Plasticizer (Palatinol 911 P)	15-40
Antioxidant (Irganox 1076)	0.2-1.2
Stabilizer (ThermCheck 1890, zinc-based)	
Phosphite (Mark 2112)	
Lubricant (polyethylene wax, AC-629)	1-4
Precipitated calcium carbonate with stearic acid coating	10-40
Wall thickness, mm	0.2-0.38
Thermal stability at 105°C, h	3000
Low temperature flexibility, °C	-40

The cable fulfills the requirements of Volkswagen and BMW standards.

Cable from blend. [Data from Thulliez, V.; Laurent, G.; Declerck, F., **US Patent 6,054,538**, Apr. 25, 2000.]

Raw material	Concentration, parts
Composition A	
Vinylidene fluoride and chlorotrifluoroethylene copolymer containing 15% of chlorotrifluoroethylene	100
Calcium molybdate	5
Stearic acid coated, precipitated calcium carbonate	0.1
Polyethylene wax	0.2
Composition B	
PVC (K=71)	100
Phthalate plasticizer	46
Lead stabilizer	6
Kaolin	7
Polyethylene wax	0.7
Antimony oxide	6
Composition C	
Copolymer of methylmethacrylate and butyl acrylate=63:37	
Proportions: A/B/C, wt%	60/40/10
Dielectric constant at 1 MHz	4.6
Tensile strength, MPa	32
Tensile strength retained after 7 days at 136°C, %	>90
Elongation at break, %	427
Limiting oxygen index, %	38

The material was extruded from 60 parts by weight of composition A, 40 parts by weight of composition B, and 10 parts by weight of the methacrylic copolymer.

Flame retardant composition. [Data from Linsky, L. A.; Andries, J. C.; Ouellette, D.; Buono, J. A.; Tao, T., **US Patent 5,886,072**, Mar. 23, 1999.]

Raw material	A	B
	Concentration, parts	
PVC	100	100
Pentaerythritol ester plasticizer (Hercoflex 707A)	33	30
Calcinated clay (SP33 from Englehard)	5	5
Aluminum trihydrate (Alcoa C710B)	70	50
Basic lead heat stabilizer (Lectro 90 TA)	6	6
Stearic acid lubricant (Hystyrene)	0.25	0.2
Antimony trioxide (flame retardant)	5	2
Brominated phthalate ester (Great Lakes DP-45)	10	15
Isodecyl diphenyl phosphate (Santicizer 2148)	5	5
Ammonium octamolybdate (flame retardant, Climax AOM)	10	10
Zinc borate (flame retardant, Climax ZB467)	2	2
Tensile strength, psi	2515	2880
Elongation, %	225	210
Brittle point, °C	0	-18
Oxygen index	49	39.5
Arapahoe smoke, %	1.8	

Lead-free composition. [Data from Mottine, J. J.; Shepherd, L., **US Patent 5,326,638**, Jul. 5, 1994.]

Raw material	Lead	Lead-free
	Concentration, parts	
PVC	100	100
Diisodecyl phthalate	30	30
Antimony trioxide	1	1
Smoke suppressant (Ongard 2)	1	1
Tribase lead stabilizer (Tribase XL)	7	
Ca/Zn stabilizer (Ferro 614W)		5
Lubricant (Rosswax 140)	0.4	
Internal lubricant (Loxiol G-16)		1.5

Lead-free composition. [Data from Mottine, J. J.; Shepherd, L., **US Patent 5,326,638**, Jul. 5, 1994.]

Raw material	Lead	Lead-free
	Concentration, parts	
External lubricant (Loxiol G-71)		0.5
Lubricant (Leaded Lub-DS-207)	0.4	
Antioxidant (Mark 5111)		0.5
Metal deactivator (Mark DSTOP)		0.25
Volume resistivity, ohm-cm	$2x10^{14}$	$12.5x10^{13}$
Dielectric constant	3.5	3.8
Thermal stability, min	34	57

Plenum cable. [Data from Krouski, P. W., **US Patent 5,227,417**, Jul. 13, 1993.]

Raw material	Concentration, parts
PVC	100
Santicizer 2148 (phosphate ester)	30
Brominated aromatic ester (Pyronil 45)	20
Epoxidized soybean oil	3
Aluminum trihydrate	30
Ammonium octamolybdate	30
Tribasic lead sulfate	7
Stearic acid	0.5
Paraffin wax (Aristowax)	0.5
Zinc molybdate (Kemgard 911C)	10
Thickness, mil	49
Oxygen index, %	52.8
Smoke density, Dm/g	21

Fire-retardant coating. [Data from Cioffi, E. A.; Hicks, H., **US Patent 5,104,735**, Apr. 14, 1992.]

Raw material	Concentration, parts
Neoprene or polydimethylsiloxane latex	1116.5
Water	272.2
Sodium silicate	1667
Fume silica	101.5
Quartz	315.2
Kaolin	101.5
Perlite	182.7
Zinc oxide	81.20
Titanium dioxide	121.8

The object of this invention is to provide a water-insoluble coating for an ignitable cable from PVC, used in naval, building and construction applications, which protects against thermal damage that causes the cable to soften, deform or ignite, yet will not significantly derate the electrical performance of cables. This invention is also useful in coating subway cables or cables in a confined space.

The composition given in the above table can be blended and made ready for use on site without premature hardening.

Cables are covered with a pasty composition. When exposed to fire, the composition forms a glass-like coating and does not ignite or fume. When heated by fire, the latex component of the composition chars, but the silicate component converts to a non-combustible, vitreous coating. The resultant fire-retardant jacket over the cable inhibits further burning and prevents re-ignition. The rigid non-permeable siliceous jacket formed by the composition helps to avoid the flow of molten cable material underneath it.

Low-smoke, flame-retardant cable. [Data from Naseem, **US Patent 4,892,683**, Jan. 9, 1990.]

Raw material	Concentration, parts
Geon 102 EP	85
Chlorinated PVC (Temprite 627X563)	15
Terpolymer of acrylic acid, ethylene, and vinyl acetate (Elvaloy 714)	12
Tribasic lead sulfate (Tribase)	10
Ammonium octamolybdate (smoke suppressant, AOM)	25
Aluminum trihydrate (Solem 932M)	42
Antioxidant (Topanol CA)	0.2
Stearic acid	0.2
Dibasic lead stearate (lubricant, DS 207)	0.2
Paraffin wax (lubricant, Aristowax 165)	0.2
Isodecyl diphenyl phosphate (Santicizer 148)	8
Brominated dioctyl phthalate (DP 45)	25
Dioctyl sebacate	5
n-octyl n-decyl trimellitate (PX 336)	12
Antimony oxide	3
Oxygen index	50
Smoke optical density (flaming)	233
Smoke optical density (smoldering)	275

Wire coating. [Data from Ogushi, Y.; Matsumoto, O., **US Patent 4,937,142**, Jun. 26, 1990.]

Raw material	Concentration, parts
PVC (polymerization degree=3,800)	100
Trioctyl trimellitate	40
Polydimethylsiloxane	1
Tribasic lead sulfate	2
Barium stearate	1
Lead stearate	0.5

This coating protects the wire from abrasion and produces light-weight coated wires.

Termite and rodent repellent coating. [Data from Ichiro, S., **US Patent 4,847,151**, Jul. 11, 1989.]

Raw material	Concentration, parts
PVC	100
DOP	50
Calcium carbonate	20
Tin stabilizer	5
Insecticide (phenylglyoxylonitrilooxime diethyl phosphorothioate, phoxim)	1
β-cyclodextrin	1.5
Reduced millet jelly	2.5

Sheath for optical cable. [Data from Eichenbaum, B. R.; Santana, M. R., **US Patent 4,859,023**, Aug. 22, 1989.]

Raw material	Concentration, parts
PVC	100
Diundecyl phthalate	30
Tribasic lead sulfate	7
Antimony trioxide	2
Dibasic lead stearate	0.4
N,N'-ethylene bis-stearamide	0.4

Blend. [Data from Chen, J. C.; Chou, R. T., **US Patent 4,778,856**, Oct. 18, 1988.]

Raw material	Concentration, parts
PVC	50
Chlorosulfonated polyethylene (43% Cl, 1% S)	25
Chlorosulfonated polyethylene (35% Cl, 1% S)	25
Ethylene/VAc/CO copolymer=66/24/10	20
Lead phosphite	5
Calcium stearate	0.5
Polyethylene	1.5
Brittle point, °C	-56.4
Volume swell (70°C/7 days/ASTM oil #3)	23.9
Tensile strength at break increase, %	220

Low voltage electrical wire with irradiation crosslinked outer coating.

[Data from Checkland, J. A.; Valois, P., **US Patent 4,310,597**, Jan. 12, 1982.]

Raw material	Concentration, parts
PVC	100
Tetraethylene glycol dimethacrylate	10
Trimethylolpropane trimethacrylate	10
Plasticizer (trioctyl trimaleate)	20
DOP	17
Stabilizer	7
Calcium carbonate	25
Antioxidant	0.3
Antimony trioxide	3

The wire is a low voltage wire for telecommunication equipment. It has a total diameter of 1 mm. The conductor is 0.6 mm in diameter. The outer layer compound is manufactured by conventional processes, for example, dry blending, pellet manufacture, extrusion, and then irradiation up to 10 Mrad dose level. The irradiation crosslinked outer layer offers sufficient abrasion resistance to protect the inner layer (polyethylene) and the conductor in usage for a wire in a switchboard or mainframe wiring. It also gives the required degree of non-flammability.

The combination of materials in the outer layer makes it easily removed to make a terminal connection, by deliberate and positive contact with a soldering iron which burns it away. On the other hand, the outer layer offers sufficient heat resistance to prevent burning when a hot soldering iron is accidentally touched against it. Thus, the wire is easily strippable for making terminal connections.

PVC cross-filler, flame retarded formulation. [Data from Jiang, Q, Keller, J, Kroushl, P, **US Patent US20130213686**, Aug. 22, 2013.]

Raw material	Concentration, parts
PVC	100
FRP 45, (brominated DOP)	60
Aluminum trihydrate	50
Huber HPSS (basic zinc molybdate)	10
Antimony trioxide	2
Ferro RC 641P (Ca/Zn stabilizer)	6
Titanium dioxide	0.5
OPE wax	0.6

4.25.3 EXXONMOBIL WIRE INSULATION FORMULAS

4.25.3.1 Formulations proposed by the raw material supplier

ExxonMobil formulas for building wire. [Data from Coaker, A. W., *J. Vinyl Additive Technol.*, **9**, 3, 108-115, 2003.]

Raw material	TW 60°C	TW-THW, 60-75°C	THWN-THNN, 75-99°C	THHN-THWM, UL83
	Parts			
PVC OxyVinyls 240	100	100	100	100
Jayflex DINP-E	62	29		
Jayflex DTDP		29	19.5	
Jayflex TINTM			23	
Jayflex 305				50
Calcinated clay	15	16	8	12
Calcium carbonate	15	15	7	
Baerostab V220 MC	4	4	3	
Pebetal				6
Antimony trioxide			1.5	4
Stearic acid	0.25	0.25	0.25	0.2

TW – moisture resistance; THW – resistant to hot water; THHN-THWM – a hybrid construction having a layer of primary vinyl insulation covered with a thin layer of secondary nylon insulation.

4.25.4 TRADITIONAL LEAD STABILIZERS IN WIRE AND CABLE

4.25.4.1 Formulations found in the open literature

Low extractable 60-75°C TW/THW insulation. [Data from Grossman, R. F., *J. Vinyl Additive Technol.*, **5**, 1, 37-39, 1999.]

Raw material	Concentration, parts
PVC	100
Diisodecyl phthalate	28
Ditridecyl phthalate	28
Calcinated clay	15
Calcium carbonate	15
Stearic acid	0.25
Tribasic lead sulfate (Halstab X- 1132)	6-7.5

Low extractable, plenum cable jacket. [Data from Grossman, R. F., *J. Vinyl Additive Technol.*, **5**, 1, 37-39, 1999.]

Raw material	Concentration, parts
PVC	100
Hercoflex 707	40
Alumina trihydrate	60
Ammonium octamolybdate	4.5
Zinc borate	9
Antimony oxide	1
Stearic acid	0.2
Antioxidant	0.2
Dibasic lead phthalate (Halstab X- 1129)	6
Tetrabasic lead fumarate (Halstab X- 1212)	6

Non-metallic insulation (NM-B) 90°C for low TLCP (Toxicity Characteristic Leaching Procedure) extractables. [Data from Grossman, R. F., *J. Vinyl Additive Technol.*, **5**, 1, 37-39, 1999.]

Raw material	Concentration, parts
PVC	100
Trioctyl trimellitate	15
Ditridecyl phthalate	30
Antioxidant	0.2
Stearic acid	0.25
Halstab X- 1129 (dibasic lead phthalate)	7-9

THHN/THWN insulation for Low TCLP extractables. [Data from Grossman, R. F., *J. Vinyl Additive Technol.*, **5**, 1, 37-39, 1999.]

Raw material	Concentration, parts
PVC	100
Trioctyl trimellitate	35
Ditridecyl phthalate	20
Calcinated clay	15
Calcium carbonate	15
Antioxidant	0.2
Stearic acid	0.2

THHN/THWN insulation for Low TCLP extractables. [Data from Grossman, R. F., *J. Vinyl Additive Technol*., **5**, 1, 37-39, 1999.]

Raw material	Concentration, parts
Antimony oxide	3-4
Halstab X- 1129 (dibasic lead phthalate)	8-9

4.25.5 CONCLUSIVE REMARKS

Typical components of formulation include:

- PVC (K=70-71 grades are most likely used in these applications),
- a large number of different plasticizers are or were used, including di-(2-ethylhexyl) phthalate, diisodecyl phthalate, diisononyl phthalate, ditridecyl phthalate, diundecyl phthalate, undecyl decyl phthalate, dioctyl sebacate, octyl decyl trimellitate, trioctyl trimellitate, isodecyl diphenyl phthalate, pentaerythritol ester, cyclohexanoic acid esters, chlorinated paraffins,
- thermal stabilizers (currently metal soaps (Ba/Ca/Zn, Ba/Zn, and Ca/Zn) are displacing formerly used lead stabilizers (tribasic lead stearate, dibasic lead stearate, tetrabasic lead fumarate); dibutyltin dilaurate was also used). Thermal stabilizers are selected regarding the type and quantity based on the type of cable and its rated service temperature, which varies in the range of 70 to 125^{o}C,
- costabilizers include epoxidized soybean oil, phosphites, antioxidants (e.g., tetrakis-[methylene-3-(3’,5’-diisobutyl-4’-hydrophenylpropionate] methane),
- calcinated clay, kaolin, calcium carbonate, and precipitated stearic acid coated calcium carbonate are used as fillers,
- lubricants include stearic acid, PE wax, and other proprietary internal and external lubricants.

Depending on the rating of a cable and its expected performance, some other additives are used, as follows:

- flame retardants (antimony trioxide, aluminum hydroxide, zinc borate, dioctyl tetrabromophthalate, PTFE micropowder),
- smoke suppressants (calcium and ammonium octamolybdate),
- components of polymer blends (nitrile rubber; chlorinated PVC; chlorinated PE; chlorosulfonated PE; EVA; vinylidene fluoride and chlorotrifluoroethylene copolymer; methylmethacrylate and butylacrylate copolymer; a terpolymer of acrylic acid, ethylene, vinyl acetate; and ethylene, vinyl acetate carbon monoxide copolymer),
- slip agents (polydimethylsiloxane, N,N’-ethylene bis-stearamide),
- insecticides and rodent repellents,

- metal deactivators.

The most important properties of the PVC coating include:

- electrical insulating performance and its long-term stability,
- durability of cable under rated conditions of use (cables are relatively very stable materials; studies of cables used for 20 and more years have shown that only a very small percentage (single digit) of active thermal stabilizer was exhausted, but a larger percentage (30% and more) of plasticizers was lost; that is why the list of current plasticizers includes many plasticizers having lower volatility; material from old cables could be used for reprocessing with addition of lost components),
- flame retardancy and smoke suppression properties are very essential in many wire and cable applications.

The most frequently encountered problems in extrusion were covered in Section 4.5 and the information is not repeated here.

4.26 GENERAL REMARKS

This chapter includes a review of many patents which contained information about formulations and the structure of their products. For the sake of the goal of this chapter, only some information included in these patents was presented but there is a wealth of information in these patents which can be useful for readers of this book. This information can be easily accessed (free of charge) from the following website addresses (URLs):

http://patft.uspto.gov/netahtml/PTO/srchnum.htm
https://patentscope.wipo.int/search/en/search.jsf/

In this chapter, US patents were preferred because they usually contain most international patents and help to avoid repetitions which are easy to make, considering the amount of data which needed to be analyzed (in total, thousands of patents have been reviewed to provide this analysis of formulations and properties).

In a few cases, formulations and/or explanations were repeated to assure that reader does not miss important information by looking for it in a section of interest.

Data in tables are centered for composition and left flushed for properties to make the search for information more accessible.