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Declarations under Rule 4.17:

- *as to applicant's entitlement to apply for and be granted a
patent (Rule 4.17(ii))*
- *as to the applicant's entitlement to claim the priority of the
earlier application (Rule 4.17(iii))*
- *of inventorship (Rule 4.17(iv))*

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(54) Title: SOFT, STRONG PLASTISOLS

(57) Abstract: A plastisol is disclosed blending together polyvinyl chloride (PVC), plasticizer, and trimethylolpropane trimethacrylate liquid resin. This acrylate unexpectedly provides a very nice haptic feel at very low durometers without loss of strength and also elongation of conventional plastisols having much higher durometers.



SOFT, STRONG PLASTISOLS

CLAIM OF PRIORITY

[0001] This application claims priority from U.S. Provisional Patent Application Serial Number 61/683081 bearing Attorney Docket Number 12012013 and filed on August 14, 2012, which is incorporated by reference.

FIELD OF THE INVENTION

[0002] The present invention relates to plastisols of polyvinyl chloride, plasticizer, and liquid acrylic resins.

BACKGROUND OF THE INVENTION

[0003] Over the past several decades, the use of polymers has transformed the world. Polymer science has rapidly evolved to make thousands of different thermoplastic and thermosetting products within the four corners of polymer physics: thermoplastic plastics, thermoplastic elastomers, thermoset plastics, and thermoset elastomers.

[0004] Industrial and commercial products are often made from poly(vinyl chloride) ("PVC") compounds in the form either of viscous liquids of unfused PVC (such as plastisols) or flexible PVC solids (such as pellets, particles, or cubes).

[0005] Along the Shore A scale of hardness, flexible PVC solids are very difficult to prepare with a Shore A hardness of less than about 70. Unfused PVC plastisols have no effective hardness until they are fused because they are liquids.

[0006] Traditionally, acrylic resins have been used in rigid PVC applications (essentially no plasticizer), in order to create a high durometer, high heat resistance PVC compound.

SUMMARY OF THE INVENTION

[0007] The problem with low durometer plastisols is that they lack tensile and tear strength necessary for many applications where the haptics of the material and physical strength are both important.

[0008] A solution to the problem is to modify the plastisol with the addition of an acrylic resin. The tensile strength of the material can be increased resulting in a more durable product with the necessary haptics. The resulting material provides a material that is still soft like human skin but has durability closer to that of real skin allowing for more realistic simulation skin to be produced for medical training purposes.

[0009] One aspect of the present invention is a polymeric plastisol, comprising (a) polyvinyl chloride; (b) plasticizer; and (c) trimethylolpropane trimethacrylate, wherein the plastisol has a durometer hardness (ASTM D2240) of less than about 12 Shore A scale and a percent elongation at break (ASTM D412) of greater than about 400%.

[00010] Another aspect of the present invention is a shaped polymeric article made from the plastisol blend described above.

[00011] A variety of articles can be prepared from the plastisol blends of the invention, as are presently made using conventional plastisol blends.

EMBODIMENTS OF THE INVENTION

[00012] Plastisol

[00013] Any currently available plastisol and any future-developed liquid plastisol is a candidate for use in the present invention.

[00014] The polymer processing art is quite familiar with vinyl plastisols. These plastisols are formed from dispersion-, microsuspension-, and emulsion-grade poly(vinyl chloride) (PVC) resins (homopolymers and copolymers) and plasticizers. Exemplary dispersion-grade PVC resins are disclosed in U.S. Pat. Nos. 4,581,413; 4,693,800; 4,939,212; and 5,290,890, among many others such as those referenced in the above four patents.

[00015] The primary liquid plasticizers used in preparing fluid plastisols from vinyl resins are organic esters of various acids such as phthalic, phosphoric, adipic, sebacic, citric, unsaturated fatty acids, and the like. Of these, the phthalate esters are most frequently used as principal plasticizers for vinyl chloride resins. Dialkyl phthalates containing medium length alkyl groups (e.g. from about 6 to about 12 carbon atoms in length) provide a good balance of plastisol properties when used in proportions from about 30 to about 300 parts by weight per 100 parts of the vinyl chloride resin powder. Specific examples of useful liquid plasticizers include dioctyl phthalate (DOP), butyl benzyl phthalate (BBP), dioctyl adipate, dibutyl sebacate, diisononyl phthalate (DINP), hydrogenated diisononyl phthalate (DINCH), hydrogenated di-2-ethylhexyl phthalate, glyceryl stearates, and combinations thereof.

[00016] Organic esters of unsaturated fatty acids are an excellent alternative to phthalate plasticizers because they are prepared from biologically renewable resources. U.S. Pat. No. 6,797,753 (Benecke et al.), incorporated by reference herein, discloses plasticizing polyvinyl chloride polymers where the plasticizers contain fatty acids derived from vegetable oils and the fatty acids are substantially fully esterified with an alcohol (monool or polyol), the fatty acids having unsaturated bonds that are substantially fully epoxidized, and wherein the fatty acids are added substantially randomly to one or more hydroxyl sites on the alcohol. These "epoxidized soyate" plasticizers derived from vegetable oil disclosed in Benecke et al., such as epoxidized pentaerythritol tetrasoyate, epoxidized propylene glycol disoyate, epoxidized ethylene glycol disoyate, epoxidized methyl soyate, and epoxidized sucrose octasoyate, are among a group of plasticizers commonly called "bioplasticizers" and are very suitable for use in the present invention.

[00017] Vinyl plastisols are typically liquid at room temperature and can be poured, pumped, sprayed or cast to make the final article, depending on the compound. These compounds can range in hardness from a hot melt plastisol, such as MB2809 plastisol from PolyOne Corporation with a 60 Shore OO

durometer, to a fishing lure plastisol with an 8 Durometer Shore A to a molding plastisol such as MB2584 plastisol also from PolyOne Corporation with a 30 Shore A durometer to a rotocasting plastisol (mostly PVC) with a 65 Durometer Shore D. Advantages of vinyl plastisol in coating and molding applications include ease of use and economy.

[00018] PolyOne Corporation (www.polyone.com) is a commercial source of liquid PVC plastisols for every consumer market. These dispersions of PVC resins in plasticizing liquids are enhanced by the addition of heat or light stabilizers, color pigments, flame retardants, blowing agents and other additives required for the intended product.

[00019] Preferred commercially available PVC plastisols include Geon™ MB2536 Flesh and MB2536A plastisol made with Geon™ 121A dispersion grade PVC and MB2809 and MB2584 plastisols having the durometers mentioned above.

[00020] Liquid Acrylic Resin

[00021] Significant to the blends of the present invention is the addition of particular acrylate, namely trimethylolpropane trimethacrylate, to provide further modification to the conventional plastisol.

[00022] Those of ordinary skill in the art would expect the addition of an acrylate to the plastisol blend to adversely affect the properties of the plastisol blend. However, surprisingly, the addition of the liquid acrylic resin has added physical strength to the plastisol blend while retaining a very low durometer. Stated another way, the addition of the liquid acrylic resin has retained physical strength while significantly softening the durometer of the plastisol blend. Either way, the combination has not been seen in the art of plastisols – soft, strong plastisols.

[00023] Trimethylolpropane trimethacrylate is a clear liquid having a glass transition temperature (T_g) of about 27 °C and a viscosity of about 44 centipoise measured at 25 °C. It is commercially available as Miramer M301

from Miwon Specialty Chemical Co. Ltd. of Republic of Korea and Sartomer 350K from Sartomer of Exton, PA, USA.

[00024] Other ingredients in the blend can include, for example, internal and other lubricants, thickeners (*e.g.*, fumed silica and calcium sulfonate), flow agents, heat stabilizers, light stabilizers, pigments (*e.g.*, carbon black, oxides, and organics), antioxidants, additional plasticizers, moisture scavengers, fillers (*e.g.*, talc and CaCO_3), and mattening agents (*e.g.*, polyurea powders and various silicas). Those skilled in the art can, without undue experimentation, select various components and various amounts of other components to fulfill desired properties.

[00025] Table 1 shows acceptable, desirable, and preferable ranges of ingredients useful in the present invention, all expressed in weight percent (wt. %) of the entire compound. The compound can comprise, consist essentially of, or consist of these ingredients.

Table 1			
Ingredient (Wt. Percent)	Acceptable	Desirable	Preferable
PVC Resin	15-25	17-23	18-22
Plasticizer(s)	20-30	22-28	24-27
Trimethylolpropane Trimethacrylate	45-55	47-53	48-52
Stabilizer(s)	0-3	0-2	0.5-1
Thickener(s)	0-5	0-3	2.5-3
Pigment(s)	0-1	0-0.5	0.1-0.2
Moisture Scavenger(s)	0-1	0-0.3	0.08-0.12

[00026] Formation of Plastisol

[00027] A low or high sheer liquid mixer with cooling jacket can be used to mix the ingredients of the blend

[00028] Initial plasticizer, resin, and thickening agents are added to the mixing vessel and blended until smooth (a Hegman value of less than 4 preferably). Once smooth, the pigment package is added to the product and allowed to disperse before charging the remaining liquids to the vessel. If the

temperature reaches 90°F (32°C), the cooling jacket is used to maintain a temperature below 100°F (37.8°C). Once the product has completely mixed and passed quality testing, it is filtered through a 100 mesh screen to remove any particles over that allowable size.

USEFULNESS OF THE INVENTION

[00029] All of the advantages and usefulness of a vinyl plastisol as disclosed in the three United States Patents above are also present in the plastisol blend of the present invention. But the liquid acrylic resin adds to those properties by making the blend softer and yet just as durable without sacrificing softness. The haptics of samples of the blend simulate the feel of human skin.

[00030] All of the conventional coating techniques for vinyl plastisols are also available for use with the soft, strong plastisols of the present invention.

[00031] Dip Coating: When the plastisol coating becomes a functional part of the mold itself, the process is called dip coating. The metal insert may or may not have a requirement for an adhesive primer. Common uses include tool handles and grips; textiles; wire grates and baskets; plating racks; conveyor hooks; and the like. Dip coating can be either hot dipping or cold dipping.

[00032] Hot Dipping: By far the most common dip-coating processing technique, hot dipping requires an item to be heated first before immersion into the plastisol. The heat causes the plastisol coating to gel on the hot form.

[00033] Cold Dipping: Preheating the metal part is not required; the amount of pickup obtained depends largely on the viscosity and thixotropic ration of the plastisol.

[00034] Molding: Several types of molding are common to plastisol applications. Slush Molding is used to produce hollow, flexible items by filling a mold with plastisol, heating sufficiently to gel a layer next to the inner mold surface, and then draining the excess plastisol. The gelled layer is then completely fused and stripped from the mold. Rotational Molding involves

hollow flexible or rigid forms with complex shapes. The process is done using a two-part mold filled with a predetermined weight of plastisol, inserted into a heated oven and rotated on two planes simultaneously. Dip Molding refers to the process of dipping a solid mold; gelling, fusing and stripping the hollow part. Open Molding is a process of molding directly in, or into, a finished article such as automotive air filters.

[00035] Other Coating: Several types of coating employ movement of the plastisol relative to the item or the item relative to the plastisol. One skilled in the art readily can employ knife coating, roll coating, reverse roll coating, etc. according to techniques taught in encyclopedias, other technical literature, or the patent literature, without undue experimentation. One reason for such easy adaptation of the mixtures of the present invention to conventional plastisol coating is that the presence of silicone does not adversely affect viscosity of the mixture.

[00036] Vinyl plastisols can be certified for end-use automotive, FDA, UL, ASTM, NSF, USDA, military, medical or customer-specific applications.

[00037] Any article that needs softness yet durability can be suitable for preparation from a vinyl plastisol of the present invention. Non-limiting examples of abrasion resistant plastisol-made articles include manikins, simulations of human body parts, medical articles, fishing lures, adult novelties, and other articles useful to have a “soft touch” tactile surface.

[00038] Further embodiments and applications of the invention are described in the following non-limiting examples.

EXAMPLES

[00039] Comparative Examples A-B and Example 1

[00040] Table 2 shows the recipe for Example 1. Table 3 shows the plastisol preparation conditions. Table 4 shows the test results as compared with Comparative Example A and Comparative Example B, both commercial plastisols from PolyOne Corporation explained in greater detail below. In order

to be tested for physical properties and durometer hardness, 50 g samples of the Comparative Examples and Example 1 were poured into a 7.5" x 7.5" x 0.1875" (19 cm x 19 cm x 0.476 cm) aluminum plate then cooked for 12 min @ 400°F (204°C). Standard Tensile bars per ASTM D412 were cut from these sheets to test tensile and elongation properties according to ASTM D412. Individual blocks of material 3" x 2" x 0.125" (7.6 cm x 5.1 cm x 0.32 cm) were prepared in an aluminum mold, and durometer was tested according to ASTM D2240.

Table 2			
Commercial Name	Chemical Name and Source	Parts	Wt. %
Synplast DOA-FDA	Diocetyl Adipate Plasticizer (PolyOne)	40	8.25%
PLASTISTAB 2335	BaZn Stabilizer (Halstab)	2	0.41%
OMG 2932	Phosphite Stabilizer (Halstab)	1	0.21%
GEON 172	PVC Resin (PolyOne)	100	20.64%
AEROSIL 200	Fumed Silica Thickener (Evonik Degussa)	1.5	0.31%
POLYCAL OF325	Calcium Oxide Moisture Scavenger (Mississippi Lime Co.)	0.5	0.10%
DINP Z DISPERSION	Fumed Silica Thickener (PolyOne)	10	2.06%
IRCOGEL 903	Calcium Sulfonate Thickener (Lubrizol)	2	0.41%
STAN-TONE HCC-27566 RED 28%	Organic Pigment (PolyOne)	0.05	0.01%
STAN-TONE HCC-27565 VIOLET	Organic Pigment (PolyOne)	0.01	0.00%
STAN-TONE HCC-31579 WHITE RCL9 DISP	Titanium Dioxide Pigment (PolyOne)	0.29	0.06%
PHTHALATE FREE RED IRON	Iron Oxide Pigment (PolyOne)	0.09	0.02%

Table 2			
Commercial Name	Chemical Name and Source	Parts	Wt. %
OXIDE DISP			
PHTHALATE FREE YELLOW IRON OXIDE DISP	Iron Oxide Pigment (PolyOne)	0.13	0.03%
Synplast DOA-FDA	Dioctyl Adipate Plasticizer (PolyOne)	60	12.38%
MESAMOLL	Alkylsulfonic Plasticizer (Lanxess)	20	4.13%
PLAS-CHEK 775	Epoxidized Soybean Oil Plasticizer (Ferro)	5	1.03%
Miramer M301	Liquid Acrylic Resin (Miwon)	242	49.94%
		484.57	100.00%

Table 3 Plastisol Preparation Conditions Example1	
Equipment Type	Post Mixer
Order of Addition	All ingredients in Table 2 listed above the pigments were added to the vessel. After mixing to a smooth consistency (a Hegman value of 4 or less), the pigments were added and mixed until well dispersed. Then, the remaining ingredients in Table 2 were added and mixed until well dispersed.
Temperature(s)	Not to Exceed 100°F (37.8°C)
RPM of Mixing	160-3000

Table 4			
Test Method Name (ASTM D412)	Example 1	Comparative Example A – MB2809	Comparative Example B – MB2584
Peak Stress (ASTM D412)	485 PSI	60 PSI	466 PSI
Break Elongation (ASTM D412)	429%	2.4%	320%
Durometer Shore A (ASTM D2240)	12		30
Durometer Shore OO (ASTM D2240)	55	60	

[00041] Table 4 shows that Example 1, having a very low durometer hardness comparable to MB2809 plastisol from PolyOne Corporation, provides physical properties comparable to MB2584 plastisol also from PolyOne Corporation. Both MB2809 and MB2584 do not contain any liquid acrylic resin.

[00042] In other words, Example 1 has all of the strength of a conventional higher durometer plastisol with a durometer as soft as a very soft commercial plastisol.

[00043] Blends containing both PVC resin and liquid acrylic resin, such as Example 1, allow for lower durometer than blends with only PVC resin, resulting in a softer, yet stronger, material. Blends of the invention are as strong as 30-40 Shore A materials but have 55 Shore OO durometer and also have higher elongation values.

[00044] Qualitatively, the resulting feel of Example 1 the product closely mimics soft silicone, a desirable property when simulating human skin.

[00045] It should be noted that while Example 1 has a formulation which does not include phthalate plasticizers, other formulations of the invention can utilize phthalate plasticizers.

[00046] The invention is not limited to the above embodiments. The claims follow.

What is claimed is:

1. A polymeric plastisol, comprising:
 - (a) polyvinyl chloride;
 - (b) plasticizer; and
 - (c) trimethylolpropane trimethacrylate,wherein the plastisol has a durometer hardness (ASTM D2240) of less than about 12 Shore A scale and a percent elongation at break (ASTM D412) of greater than about 400%.
2. The plastisol of Claim 1, wherein the polyvinyl chloride is a dispersion-grade homopolymer or copolymer, a microsuspension-grade homopolymer or copolymer, or an emulsion-grade homopolymer or copolymer.
3. The plastisol of Claim 1 or Claim 2, wherein the plasticizer is an organic ester of an acid selected from the group consisting of phthalic acids, phosphoric acids, adipic acid, sebacic acid, citric acid, unsaturated fatty acids, and combinations thereof.
4. The plastisol of Claim 3, wherein the plasticizer is selected from the group consisting of dioctyl phthalate (DOP), butyl benzyl phthalate (BBP), dioctyl adipate, dibutyl sebacate, diisononyl phthalate (DINP), hydrogenated diisononyl phthalate (DINCH), hydrogenated di-2-ethylhexyl phthalate, glyceryl stearates, epoxidized pentaerythritol tetrasoyate, epoxidized propylene glycol disoyate, epoxidized ethylene glycol disoyate, epoxidized methyl soyate, epoxidized sucrose octasoyate, and combinations thereof.
5. The plastisol of any one of the above Claims, wherein the trimethylolpropane trimethacrylate has a glass transition temperature (T_g) of about 27 °C and a viscosity of about 44 centipoise measured at 25 °C.

6. The plastisol of any one of the above Claims, wherein the plastisol further comprises internal lubricants, thickeners, flow agents, heat stabilizers, light stabilizers, pigments, antioxidants, additional plasticizers, moisture scavengers, fillers, or mattening agents.

7. The plastisol of any one of the above Claims, wherein the weight percent of ingredients of the plastisol comprise

Polyvinyl Chloride	15-25
Plasticizer(s)	20-30
Trimethylolpropane Trimethacrylate	45-55
Stabilizer(s)	0-3
Thickener(s)	0-5
Pigment(s)	0-1
Moisture Scavenger(s)	0-1

8. A plastic article formed by a coating of the plastisol of any one of Claims 1-7.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/054720**A. CLASSIFICATION OF SUBJECT MATTER****C08L 27/06(2006.01)i, C08K 5/10(2006.01)i, C08K 5/05(2006.01)i, C08J 5/00(2006.01)i, C08J 7/04(2006.01)i**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08L 27/06; C08K 5/00; C08K 5/10; C08K 5/05; C08J 5/00; C08J 7/04

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & Keywords: polyvinyl chloride, trimethylolpropane trimethacrylate, liquid acrylic resin, plastisol

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ZADHOUSH, A. et al., "Crosslinking of plasticized PVC used in coated fabrics", Journal of Vinyl and Additive Technology 2009, Vol. 15, Issue 2, pages 108-112. See pages 108-111; Table 1.	1-4
X	YANEZ-FLORES, ISAURA G. et al., "Peroxide crosslinking of PVC foam formulations", European Polymer Journal 2000, Vol. 36, Issue 10, pages 2235-2241. See pages 2235-2237.	1-4
X	TAI, HORNG-JER, "Processing and properties of high-temperature creep-resistant PVC plastisols", Polymer Engineering and Science 1999, Vol. 39, No. 7, pages 1320-1327. See abstract; page 1321-1322; Table 1-2.	1-4
A	BOUDHANI, HASSANE et al., "Viscoelasticity and mechanical properties of reactive PVC plastisols", Polymer Engineering and Science 2009, Vol. 49, Issue 6, pages 1089-1098. See abstract; pages 1089-1093; Table 1; Figures 3-4.	1-4
A	US 5137952 A (MILLER, HENRY C. et al.) 11 August 1992 See abstract; Examples 1-8.	1-4



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

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Name and mailing address of the ISA/KR

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INTERNATIONAL SEARCH REPORTInternational application No.
PCT/US2013/054720**Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 5-8
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2013/054720

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5137952 A	11/08/1992	EP 0534847 A1 EP 0534847 B1	31/03/1993 27/12/1996