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MODIFIED POLYVINYL CHLORIDE COMPOSITIONS, METHODS FOR THEIR USE AND PREPARATION AND ARTICLES PRODUCED THEREFROM

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1 Claim

ABSTRACT OF THE DISCLOSURE

A process for applying a plastic label to a supporting substrate and the plastic label capable of being applied, said process comprising applying a refusible adhesive to one side of a label prepared from a modified polyvinyl chloride plastisol composition; curing said label containing said adhesive coated on one side thereof; applying said label having said adhesive coating thereon to a supporting substrate with said adhesive in contact therewith; and applying sufficient heat and pressure to the label to cause the adhesive to refuse so as to permit the bonding of the label to the supporting substrate. A further process comprises applying a plastic label to a supporting substrate by partially curing at least a portion of a label prepared from modified polyvinyl chloride plastisol; applying said label to a supporting substrate with the partially cured portion in contact therewith; and subjecting said label and supporting substrate to sufficient heat and pressure to bond said label to said supporting substrate.

This application is a continuation-in-part of copending application Ser. No. 311,318, filed on Sept. 25, 1963, now abandoned.

This invention relates to modified polyvinyl chloride compositions, to methods for their use and preparation and to articles produced therefrom. More particularly, it relates to novel polyvinyl chloride compositions which have particular utility in connection with the preparation of labels and to methods for using and preparing such compositions and to articles produced therefrom.

Various sorts of identifying, advertising and information conveying means have been used with garments, fabric materials and the like. For example, markers, symbols or insignia may be used for the purpose of labeling a garment by setting forth the manufacturer, designer, styling, authenticity, etc. In another common usage an insignia label or other marking might indicate membership or association with an organization such as those used for school letters, emblems used on shirts for bowling teams, etc. Still another very widespread usage comprises military or company insignia, indicating both the identity of the organization and also the rank or position of the wearer. For children's wear the pictures or names of prominent athletes, team names or slogans are frequently displayed. Myriads of other specific uses could be mentioned but will be apparent to those skilled in the art from the preceding. These labels, emblems, pictures, insignia, etc., are usually embroidered or prepared in some similar manner from thread or yarn.

Customarily, the labels, emblems, insignia, etc. (hereinafter collectively referred to as labels), are attached to a garment by sewing and have proven relatively serviceable. However, the cost of the embroidered labels themselves and time and labor required for attaching them to a garment make this form of labeling relatively expensive.

There are commercially available transfer type labels based on heat application of a plastic material to a fabric substrate. However, these labels lack the desired serviceability because of the destructive effects of industrial laundering and dry cleaning detergents and chemical cleaning fluids. After a few cycles of cleaning, the label usually disintegrates and is removed from the fabric. Although some types of transfer labels may withstand home laundering, the higher temperatures and more caustic, industrial laundering cause degradation and loss of the label. As a result, plastic transfer labels have not, to date, achieved significant commercial usage.

The use of plastic materials for use in transfer and similar types of labels would be very desirable since the costly embroidering could be eliminated. If such a process were available the plastic material could be formed by molding, etc. into desired designs which would compare very favorably with embroidered designs.

If plastic materials are to be used in such labels, unique properties are required of the plastic. It must resist laundering for many cycles at temperatures up to 190° F. in caustic detergents. Furthermore, no softening or degradation can occur when the material is subjected to dry cleaning in industrial type cleaning solvents such as perchloroethylene. In addition, the material must not soften, flow or smear when subjected to normal ironing temperatures of 300° to 325° F. maximum. The plastic label must not lose its adhesion to a wide variety of fabric substrates during normal wear and cleaning. The plastic material, in addition to having good performance properties, must possess formability, i.e., the fabrication of the designs of the labels must be practical and inexpensive. A wide range of colors, textures and designs should be possible in the use of the plastic material.

The present invention provides new and improved plastic labels, processes for producing them, and novel compositions from which they can be made. The improved label overcomes all the aforementioned difficulties and is durable and resistant to the action of detergents and cleaning fluids. It can also effectively withstand normal ironing temperatures and generally has all the unique properties for plastic transfer labels mentioned above.

It is accordingly a principal object of the present invention to provide new and improved plastic labels, processes for producing them and novel compositions from which they can be made.

It is another important object of the present invention to provide new and improved plastic labels which are particularly resistant to laundering and dry cleaning yet which possess the many advantages of prior art labels.

It is still a further important object of the present invention to provide new and improved plastic labels which are particularly well adapted for use as transfer labels.

It is still a further important object of the present invention to provide novel plastic labels which have significantly improved shelf-life and yet which may still be readily and effectively bonded to an ultimate surrounding substrate.

These and other important objects and advantages of the present invention will become more apparent through reference to the ensuing description and appended claims.

In accordance with the present invention, a novel plastic material is provided which is particularly well adapted for the fabrication of plastic labels of the transfer and other types and which overcomes the major difficulties associated with prior art plastic labels heretofore used. The novel composition making possible these advantages is comprised of four essential ingredients including (a) a polyvinyl chloride resin, (b) a linear or branched chain aliphatic epoxide containing more than two functional sites, (c) an organic acid anhydride containing at least

two functional sites and (d) a non-reactive plasticizer which is compatible with the remaining ingredients of said composition.

In the preferred embodiment of this invention, the formulations used to form the plastic labels are of the plastisol type. Plastisols are suspensions of finely ground particles of resinous polymers in a compatible fluid plasticizer. When heated to the proper temperature, the plastisol changes into a homogeneous rubber-like material which is particularly adapted for use in formation of labels.

Various synthetic resins of the thermoplastic type are suitable to be made into labels. Particularly suitable because of their excellent resistance to caustic solutions encountered in industrial laundering are the vinyl plastisols. Vinyl plastisols, however, have extremely poor resistance to dry cleaning solvents, especially the chlorinated types, which have a tendency to extract the plasticizer from fused plastisols producing a rigid, brittle material. Considerable shrinkage occurs, which would produce puckering of the fabric to which the label is attached.

In addition to the foregoing, normal fused vinyl plastisols soften at temperatures above 200° F. and melt at about 275–300° F. Thus, they cannot be used in making plastic transfer labels of the type heretofore mentioned since they would not resist ironing temperatures.

The present invention makes possible on an extremely practicable basis the use of vinyl resins to form plastic labels, of the transfer-type as well as other varieties, by incorporating in the label formulation materials of the type heretofore mentioned. The use of such materials in label manufacture results in the reduction of plasticizer extraction losses and a significant increase in the temperature resistance of the label.

The significant increase in the solvent extraction and temperature resistance of the polyvinyl chloride formulation of the present invention is made possible by means of the epoxide and acid anhydride components of the formulation. The epoxide component serves two main purposes in the formulation. Its primary purpose is to provide reactive sites for producing a crosslinked resin when reacted with the acid anhydride component of the formulation. When sufficient crosslinking takes place, the non-reactive plasticizer component of the formulation (whose purpose will be discussed below) is adequately trapped within the formulation to prevent its solvent extraction, such crosslinking also serving to increase the resistance of the material to temperatures such as may be encountered during pressing on industrial steam presses and the like. The second purpose of the epoxide component is that it serves as an excellent temperature and light stabilizer for the polyvinyl chloride resin component used in such formulation.

The acid anhydride is used in the formulation of the present invention to react with the epoxide to form the desired crosslinked structure necessary to provide the desired heat resistance and resistance to solvent extraction.

Because polyvinyl chloride is a linear thermoplastic synthetic resin which is a hard, horny material in the unplasticized state, it is necessary to include in the formulation of the present invention a non-reactive plasticizer compatible with the other formulation ingredients to produce a soft, flexible material having many desirable properties. While the incorporation of such a plasticizer does tend to make the formulation subject to extraction and softening at elevated temperatures, a compromise must be made to give the plastic formulation some flexibility in order to obtain a material satisfactory for its intended use in fabricating labels. The incorporation of moderate amounts of such a non-reactive plasticizer produces the flexibility desired without grossly reducing the solvent and temperature resistance of the fused plastic material.

The polyvinyl chloride component of the formulation described above is, in a preferred embodiment of the present invention, a homopolymer of vinyl chloride. It is within the contemplation of the present invention, how-

ever, to use copolymers of vinyl chloride with other materials such, for example, as vinylidene chloride and vinyl acetate. The use of such copolymers will permit variations in the physical properties of the formulation. Thus, the use of increasing amounts of vinyl acetate will soften the plastisol whereas increasing the amount of vinylidene chloride will increase its hardness and reduce compatibility. As a result, the dominant portion of such copolymers should be vinyl chloride. [When used in the claims, the term "polyvinyl chloride resin" shall be considered to include not only homopolymers of vinyl chloride but copolymers of vinyl chloride such as is described above wherein the vinyl chloride comprises the dominant portion of such copolymers.] The molecular weight of the vinyl chloride polymer component is desirably about 20,000–60,000 with about 40,000–60,000 being preferred, though the present invention is not limited to materials of these molecular weight ranges.

The epoxide components of the present formulations are particularly advantageously employed for their intended purpose since they produce no deleterious by-products when crosslinked with the acid anhydride component. As previously indicated, the epoxide is a linear or branched chain aliphatic epoxide and must contain more than two functional sites (though it should be noted that the epoxide can contain aromatic groups if the resultant compound is compatible with plastisol). The epoxide should be a fluid or semi-fluid which is mixable with the other components of the formulations of the present invention. An extremely effective epoxide for this purpose is an epoxidized tall oil containing four to five reactive epoxide groups per molecule sold by Swift and Company under the designation "Epoxol 9-5." This epoxide has an epoxide oxygen content of at least 9% by weight. Other epoxy materials are epoxidized plasticizers commercially available under the designation "Paraplex G-62" sold by the Rohm and Haas Company and "Estynox 400" sold by the Baker Castor Oil Company. Aliphatic diepoxides such as the Dow Chemical Company X-2670 series of epoxide resins may also be used, but the compatibility of these resins with non-reactive plasticizers is not as good as that of the other epoxides mentioned. Generally speaking, epoxides having a molecular weight of about 500–2,000 are advantageously usable in the formulations of the present invention, with a molecular weight of about 700–1,000 being preferred.

Any organic acid anhydride material which contains at least two functional groups and which will react with the epoxide component of the plastic formulation to form a crosslinked structure is usable in the formulations of the present invention. Examples of suitable anhydrides for this purpose are pyromellitic, phthalic and hexahydrophthalic anhydrides. As will be apparent, the particular anhydride utilized will depend upon the identity of the epoxide component of the plastic formulation. The prime consideration affecting such choice is the crosslink density desired in the final crosslinked product which is obtained from such formulation. If the crosslink density is too high, the resultant material is extremely brittle and not satisfactory for label use; too light a crosslink density, on the other hand, does not adequately trap the non-reactive plasticizer, which will be subsequently subject to solvent extraction in chlorinated dry cleaning solvents. In addition, if the crosslink density is not sufficiently high, the resistance of the label material to temperatures encountered during pressing on industrial steam presses will not be adequate and the label will soften and stick to the press.

Most desirable results in terms of the crosslink density of the final product are obtained when the average combined functionality of the epoxide and anhydride components is approximately 3. This average functionality may be readily controlled for a given epoxide material through judicious choice of the anhydride component of the plastic formulation. Thus, in the case of the "Epoxol 9-5" epoxide previously mentioned (which has 4 to 5 func-

tional sites), the average functionality of the combined epoxide-anhydride mixture may be controlled by using a material such as a pyromellitic dianhydride (which is a high functionality material having four functional groups per molecule) in admixture with a material such as hexahydrophthalic anhydride (a material of low functionality having two functional groups per molecule). Still other mixtures of poly and mono-anhydrides can be used for this purpose. As will be apparent, by varying the degree of crosslinking produced in the final product (viz, by varying the functionality of the combined epoxy-anhydride mixture) one can vary the temperature resistance, solvent resistance and rigidity of the final plastic product.

A great variety of non-reactive plasticizers may be usable as the fourth component of the plastic composition of the present invention. Such plasticizers include the phthalate esters, aliphatic diesters and polymeric plasticizers, merely to mention a few. Since labels made from the composition of the present invention must resist the effects of dry cleaning solvents, especially perchloroethylene, the polymeric plasticizers are preferred. Polymeric plasticizers such as "Paraplex G-25" (Rohm and Haas), a polyester of about 8,000 molecular weight, is particularly desirable for use in formulating compositions within the present invention. Another good non-reactive plasticizer is "Admex 760," a polymeric ester type of plasticizer of relatively high molecular weight manufactured by The Archer-Daniels-Midland Corporation. Exemplary of other plasticizers usable in the plastic compositions of the present invention are diesterified carboxylic acids such as dibutyl sebacate and diesterified aromatic dicarboxylic acids such as dibutyl phthalate.

In addition to the four basic ingredients of the novel formulations of the present invention, such plastic formulations may also contain other ingredients so as to impart specific desired properties to them. For example, a suitable pigment adapted to develop the desired color and optical properties of the label to be made from the formulation may be incorporated in it. The pigments used in these formulations must, of course, be resisted to extraction by dry cleaning solvents, resistant to laundering, and must be stable to temperatures in the order of 375-400° F. (the temperature commonly employed in the manufacture of labels from the present formulations). In addition, such pigments must withstand temperatures encountered in the pressing of a garment bearing the label after laundering or dry cleaning. While a great variety of pigments may be thus employed, the most satisfactory pigments are those based on cadmium sulfide, stable metal oxides, mixtures of stable metal oxides and sulfides and organic pigments based on metal containing phthalocyanines.

Light and heat stabilizers for improving the lifetime of the label under laundering and dry cleaning conditions as well as those encountered in outdoor exposure may also be included. A typical example of such a compound is the organo-tin compound dibutyltin dilaurate.

Since, as will be described hereinafter, one of the techniques of applying the novel plastic material of the present invention to a supporting surface for formation of a label is by silk screen techniques, materials may be incorporated in such formulations to improve their flow characteristics. Such a material is Alcolac Z-6 Lecithin, which is a proprietary partially hydroxylated lecithin of the American Lecithin Company. Lecithin can be described as one of several waxy, hygroscopic phosphatides which are found in both animal and plant organisms.

Modification of the flow properties of the formulation for application by silk screening techniques or the like may also be affected by adding small quantities of a material which imparts thixotropic properties to the mixture. Certain heavy metal stearates or a silica material such as "Cab-O-Sil," a product of the Cabot Corporation, are suitable for this purpose.

Non-reacting diluents to control the viscosity of the

plastisol mixture so that it can be readily passed through a silk screen (when that technique is employed) during production of a label may also be incorporated in the formulations of the present invention. An extremely effective diluent for this purpose is xylene.

The rate of reaction of the anhydrides with the epoxides can be increased by addition of catalysts to the reaction mixture, such as α -methylbenzyltrimethylamine or other tertiary amines. Quaternary amines such as benzyltrimethylammonium chloride are more active catalysts although such materials may cause some discoloration of the plastisol. If used, a material such as benzyltrimethylammonium chloride is effective in the form of a 60% aqueous solution.

For best results, all materials used in the formulations of the present invention are milled to improve dispersion and mixing.

Polyvinyl chloride plastisols prepared in accordance with the present invention can be cured at temperatures ranging from 325-400° F. requiring times of 30 seconds to 5 minutes to effect such cure. The resulting plastic material subjected to a 24 hour immersion in perchloroethylene shows only a 7% weight loss in comparison with a 42% weight loss for a polyvinyl chloride material without the crosslinked additives of the formulations of the present invention. No flow or smear was detected in the crosslinked formulation at hot ironed temperatures up to 325° F.

The formulations of the present invention may be employed in a variety of techniques to make labels and the like. In a first such technique, which is adapted particularly for the manufacture of transfer labels, the plastisol fluid of the present invention is screened onto a transfer substrate through a reverse pattern silk screen technique. After each screening (different colors and patterns to develop the desired item are employed) the plastisol is heated sufficiently to partially fuse it. The fusion effected upon the application of each layer is merely that necessary to permit handling of the material without excessive tackiness, but not enough to prevent good adhesion between layers. After all the layers have been applied (in a conventional label sufficient layers will be applied to create a label of approximately 3-5 mils in thickness), the partially fused plastisol coatings are reheated to complete the crosslinking reaction. When this has been done, a final layer of the plastisol material is then applied but this layer is only partially fused so that it will effectively serve as an adhesive to permit bonding of the label to the ultimate supporting substrate to which the label is to be affixed.

The label thus prepared is placed on the desired fabric substrate with the partially cured plastisol face down and pressed at 350-400° F. and 5-15 p.s.i. to perform the transfer and bonding operation. After cooling, the transfer substrate is removed to expose the completed label.

As will be apparent, the transfer substrate must be a reasonably non-adherent surface such as coated foil, Mylar or coated paper stock. A wide range of textures can be developed on the label by using a correspondingly textured transfer surface.

In the process described above, it is essential that the reaction of the modifying agents (the epoxide-acid anhydride mixture) take place after the fusion of the resin and plasticizer to form the plastisol. The reaction should occur rapidly after the fusion but be capable of being stopped prior to the point where complete reaction takes place. If the reaction goes to completion, it would be impossible to transfer the label to a fabric substrate with heat alone. Sufficient meltability must be retained in the modified plastisol to permit the label to be transferred to the fabric. Enough flow must take place to allow impregnation of the fabric and resultant development of adhesion. The final cure of at least the last layer of the

plastisol material should take place when the label is heat transferred to the fabric substrate.

The formulations described above and labels made from them are extremely effective in eliminating the major problems faced by the prior art in this field in connection with transfer labels. Such formulations and labels are particularly advantageous where the labels are to be used within a reasonable time after their manufacture. It is within the contemplation of the present invention, however, to provide a technique alternative to the transfer technique described above in those situations where long shelf life of the label product is a necessity, since exposure of the partially cured transfer labels prepared by the foregoing technique to the ambient may result in the curing of the partially fused plastisol material to a point such that such material will not flow effectively to permit proper bonding to the ultimate fabric substrate.

In this alternate technique, the plastisol layers applied to the transfer substrate are partially fused as before. After the application of the last plastisol layer, an adhesive layer of a reusable material is screened onto the label and the entire substrate and label assembly is passed through an oven to complete the fusion (curing) operation. The temperature and time used in curing this label is sufficient to provide complete fusion of all portions of the label, including the adhesive layer. This procedure differs from that first described above in that the latter involves only partial fusion of the last layer applied to the label so that that last layer could serve as an adhesive with final fusion taking place at the time of the application of the label to the ultimate supporting substrate. By utilizing a reusable adhesive layer as the last layer of the label in this second technique, the entire label may be cured at its time of manufacture, which will effectively make available a label with an almost indefinite shelf life since shelf-curing no longer presents a problem.

A particularly effective adhesive material for use in connection with the second technique is one comprising a copolymer of vinyl chloride and vinyl acetate having a molecular weight of about 20,000 (which copolymer is compatible with the underlying polyvinyl plastisol), with a polymeric polyester plasticizer such as Admex 760, and a small quantity of a monomeric plasticizer such as dioctylphthalate.

Still additional adhesive materials may be used to secure the novel labels of the present invention to their ultimate supporting substrates. For example, the class of adhesives known as urethane adhesives may be employed to bond the above-described labels to a suitable fabric substrate. This type of adhesive is derived from organic diisocyanates and organic polyols. A typical urethane adhesive can consist of a prepolymer prepared from toluene diisocyanate and a polypropylene glycol having a molecular weight of about 400. These two components are reacted in nearly stoichiometric quantities so that the polymer is terminated with isocyanate groups. This prepolymer can then be mixed with an appropriate amount of a second polyol to finish the reaction. A fluid adhesive is obtained which can be applied by brush or spray to the reverse side of the cured label and the composite directly applied to the fabric substrate. While permitting the securing of such labels to a supporting substrate, this particular procedure would require a rather long cure time under pressure and is not as economically feasible as is the polyvinyl chloride based adhesive previously described.

An alternative approach involves the preparation of a high molecular weight linear polyurethane derived again from diisocyanates and appropriate polyols to form a rubber-like material at room temperature but one which will soften and flow under temperatures in the order of 275-375° F. This type of adhesive may be applied to the previously formed label during the manu-

facturing operation as previously described in connection with the polyvinyl chloride based adhesive material and the entire assembly cured at that time. The adhesive will soften and flow at the time the label is applied under heat and pressure to the desired fabric substrate.

A particularly promising adhesive derived from urethanes is one made from a hydroxy-terminated prepolymer mixed with a phenol blocked diisocyanate. Such phenol blocked diisocyanates are made by reacting stoichiometric quantities of phenol with the diisocyanates to produce a phenol urethane which is stable at room temperature but which, on exposure to temperatures above 200° F., disassociates to release free-reactive isocyanate groups. This prepolymer-blocked isocyanate mixture may be applied to the reverse side of a pre-cured polyvinyl chloride label prepared as previously described and allowed to dry to form a tack-free surface. When exposed to temperatures and pressures in the range of 350-400° F. and about 5-15 p.s.i., the urethane adhesive will decompose and cure in a relatively short time (3-5 minutes) to provide a good bond to the fabric substrate. Once again, this system is not as effective as the polyvinyl chloride system previously described in that longer press cure times are required than may be used with the polyvinyl chloride based adhesive.

Aside from the advantages obtained from the second technique described above in connection with increased shelf life, the use of a fully cured label makes possible the lifting of the label from the transfer substrate on which it is formed for inspection purposes, prior to its application to the final fabric substrate. This label may be applied by placing it on the final fabric substrate, covering it with a release sheet of suitable material such as Teflon, untreated cellophane or silicone-treated paper and the application of the proper amount of heat and pressure. Thus, this technique makes possible the manufacture of non-transfer-type labels.

Since labels prepared from the plastic formulations of the present invention may be adapted to be subjected to both dry cleaning and laundering operations, it may be desirable for such purpose to compose such formulations with a view toward optimizing the resistance obtainable under laundering and dry cleaning conditions. An excellent formulation for this purpose comprises a modified plastisol as set forth in Example 1:

EXAMPLE 1

	Parts by weight
PVC (Stir-in-grade, having a molecular weight between 20,000-40,000)	120
Linear diepoxide (molecular weight 700-1,000)	50
Primary plasticizer, i.e., dioctylphthalate	40
Pyromellitic dianhydride	4

The components are mixed together and milled to form a fluid suspension. The plastisol upon curing at about 325° F. for approximately 5 minutes produces a relatively flexible material with high resistance to perchloroethylene and hot iron temperatures up to 325° F.

Additional examples of formulations optimized for combined dry cleaning and laundering resistance are set forth below in Examples 2-4:

EXAMPLE 2

	Parts by weight
PVC-71 a high molecular weight (between 20,000-40,000) dispersion resin of polyvinyl chloride (Diamond Alkali Company)	100
Epoxol 9-5 (Swift and Company)	50
Hexahydrophthalic anhydride	40
α -Methylbenzylidimethylamine	2.0

This formulation reacts slowly to produce a relatively flexible material with only moderate resistance to solvent extraction when cured for 10 minutes at 360° F. Increasing the curing time reduces the extraction loss.

EXAMPLE 3

	Parts by weight
PVC-71	100
Epoxol 9-5	50
Hexahydrophthalic anhydride	25
Pyromellitic dianhydride	10
α -Methylbenzyl dimethylamine	2.0

This formulation cured very rapidly at 360° F. to provide a rigid plastic with 2% weight loss on extraction in perchloroethylene. The material would not transfer onto the fabric because it did not melt or flow at 400° F. Such a formulation would be quite satisfactory for direct application to fabric.

EXAMPLE 4

A more fluid mixture can be made by using a liquid anhydride such as methyl-endomethylene tetrahydrophthalic anhydride or endomethylene tetrahydrophthalic anhydride in place of the hexahydrophthalic anhydride.

	Parts by weight
PVC-71	100
Epoxol 9-5	50
Endomethylene tetrahydrophthalic anhydride	25
Pyromellitic dianhydride	10
α -Methylbenzyl dimethylamine	2.0

This formulation produces a cured material similar in properties to that of Example 3. It is not as color stable at fusion temperatures and tends to yellow more, creating difficulties in producing a pure white pigmented material.

Composite formulations such as are described above are particularly useful in situations in which, after the components of the formulation are mixed together, the formulation is converted into labels within a reasonably brief period of time. In situations in which there is a long interval between the mixture of the formulation components and the conversion of the formulation into labels, however, a spontaneous reaction between the epoxide and acid anhydride components of the formulation may take place, resulting in possible impairment of the formulation for its intended use. This problem may be obviated by dividing the components of the formulation into a plurality of portions with the reactive components of the formulation being separated from one another until it is time to use the formulation, at which time the separate portions may be mixed together for application to the desired supporting substrate.

Example 5 below sets forth a formulation for use in accordance with the present invention which is made up of two separate portions, one designated as part A and the other as part B. As will be noted, part A contains the polyvinyl chloride resin and the epoxide while part B contains the acid anhydride and the non-reactive plasticizer.

EXAMPLE 5

Part A

Components:	Weight percent
Pigment	14.7
Epoxol 9-5	27.3
PVC-71	49.9
Dibutyltin dilaurate	0.6
Alcolec Z-6 lecithin	0.5
Xylene	7.0

Part B

Pyromellitic dianhydride	23.8
Hexahydrophthalic anhydride	49.9
Admex 760 plasticizer	25.9
Benzyltrimethylammonium chloride (60 percent aqueous solution)	1.3

The two component portions of the formulation of this example are mixed together using 100 parts by weight of part A and 22.1 parts by weight of part B, such ratio

corresponding to 81.9% part A and 18.1% part B. This formulation is specifically adapted for the preparation of labels which are particularly resistant to the conditions engaged in laundering. In order to optimize the formulation for this purpose, its resistance to dry cleaning conditions is diminished somewhat.

Example 6 sets forth a two-part formulation which has been optimized to adapt the material particularly for the manufacture of labels which are especially resistant to dry cleaning in chlorinated solvents.

EXAMPLE 6

Part A

Components:	Weight percent
Harshaw Zulu Blue No. 4851 (pigment)	2.80
Lamp Black (pigment)	0.05
Du Pont Ti-Pure MR-610 (pigment)	0.20
Epoxol 9-5 plasticizer	31.30
Dibutyltin dilaurate	0.65
PVC-71	57.50
Alcolec Z-6 lecithin	0.50
Xylene	7.00

Part B

Pyromellitic dianhydride	11.2
Hexahydrophthalic anhydride	24.0
Admex 760 plasticizer	63.8
Benzyltrimethylammonium chloride (60 percent aqueous solution)	1.0

The ink formulation is prepared by mixing 100 parts by weight of part A with 35.8 parts by weight of part B. This mixture corresponds to 73.6 weight percent of part A and 26.4 weight percent of part B.

Once again, the optimization of the formulation for maximum resistance to dry cleaning conditions necessarily reduces somewhat the resistance of the formulation and labels made therefrom to laundering operations.

As will be apparent, the particular formulation to be used in a given situation will depend entirely upon the ultimate use to which the formulation is to be put.

Generally speaking, the quantity of each of the four main ingredients (the polyvinyl chloride resin, the epoxide, the acid anhydride and the non-reactive plasticizer) may be varied in the formulations previously described within a range of about $\pm 10\%$ by weight of the quantities recited for such ingredients, the desirable properties obtained from the formulations of the present invention still being obtained within this degree of variation.

While the present invention has been described primarily in conjunction with the use of fabric substrates, it will be recognized that the invention is not restricted to such substrates. Other flexible substrates may be used, including but not restricted to leather, plastics, fabrics previously coated or treated with resins, etc. Furthermore, while the primary use of the invention lies in the use of labels and the like for flexible materials to be subjected to cleaning operations and/or the elements, it is also within the purview of the present invention to apply such labels and the like to inflexible materials which may or may not constitute a fabric substrate, such for example as wood, glass and the like.

In the foregoing description, the preferred means of application of the plastisol formulation to a supporting substrate was by means of a reverse pattern screen. As will be apparent to those skilled in the art, at least when using the embodiment described above in which the formulation is fully cured (rather than partially cured), it may be desirable to print the label "face up" to create certain special effects, since the cured label may be lifted from its supporting substrate prior to application to the final substrate to which the label is to be bonded. Similarly, while silk screen techniques are preferred for fabricating labels in accordance with the present invention, other techniques, such as knife and roller coating methods, may be employed.

While the formulations of the present invention are particularly well adapted to the fabrication of labels which are to be applied to an ultimate substrate by a combined heat and pressure process, labels made from such formulations can, if desired, be applied to a non-woven substrate by a sewing process or the like, since advantages will still be obtained from the highly resistant formulation from which the label is prepared. Such an application would be of great commercial value where permanent identification is not necessarily desirable, such as in the case of industrial rental laundries.

Alternatively, one can apply the formulations of the present invention in the desired label pattern directly onto the ultimate supporting substrate, as by silk-screening or other suitable technique. For example, the formulation can be silk-screened directly onto a non-woven fabric base. The composite is then placed in an oven for from 1 to 2 minutes at about 350-400° F. The resultant product is an inexpensive fabric label which will withstand numerous commercial washings, pressings and dry cleanings.

As will be apparent to those skilled in the art, the particular method of applying heat to the label at the time of its bonding to its ultimate supporting substrate is not particularly critical. Thus, one can use a press adapted to apply the necessary pressure to the label on its supporting substrate which press is provided with heating elements to raise it to the desired temperature. Alternatively, other forms of heating such as high frequency dielectric heating techniques may be employed for the purpose.

The formulations described previously and constituting the most important inventive aspect of the present application are, as stated, formed of four essential ingredients including a polyvinyl chloride resin, and epoxide, an acid anhydride and a non-reactive plasticizer. The last-mentioned ingredient is required to provide flexibility in the more highly crosslinked, heat resistant laundry formulations and is also needed in dry cleaning formulations to provide greater resistance to solvents conventionally used (such as perchloroethylene). There are certain applications, however (such as in dry cleaning, where hydrocarbon solvents such as Stoddard Solvent are used), where the formulations may advantageously have the non-reactive plasticizer omitted (see Examples 2-4). It is within the contemplation of the present invention to include such three component formulations, though it is to be understood that the preferred and more highly versatile and superior formulations are those with the four essential components indicated.

The invention may be embodied in other specific forms without departing from the spirit or essential characteristics thereof. The present embodiments are therefore to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claim rather than by the foregoing description, and all changes which come within the meaning and range of equivalency of the claim are therefore intended to be embraced therein.

What is claimed and desired to be secured by United States Letters Patent is,

1. A process for preparing and applying a heat and solvent resistive label to a fabric substrate comprising the following steps: preparing a plastisol composition comprising the following ingredients in the following proportions by weight 100 to 120 parts of a polyvinyl chloride resin selected from the groups consisting of homo polymers of polyvinyl chloride and copolymers of vinyl chloride and vinyl acetate, said polymers having a molecular weight of from 20,000 to 60,000; 45 to 55 parts of epoxide selected from the group consisting of linear and branch chain epoxides having a molecular weight of from 500 to 2,000 and having approximately 4 to 5 epoxide groups per molecule; said plastisol further containing 35 to 40 parts of an anhydride selected from the group consisting of pyromellitic dianhydride, hexahydrophthalic anhydride, phthalic anhydride, and from 36 to 44 parts of a non-reactive plasticizer; applying the plastisol composition onto a transfer substrate and heating sufficiently to effect a partial curing of the plastisol label composition; applying a refusable adhesive layer onto the partially cured label; passing the adhesive coated, partially-cured label through an oven at a temperature of from 325° F. to 400° F. to complete the curing of the label composition; applying said label with said adhesive coating thereon to a fabric substrate with the adhesive in contact with the fabric; and subjecting it to heat and pressure to refuse the adhesive composition and permit bonding to said fabric substrate.

References Cited

UNITED STATES PATENTS

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161-256, 406; 117-3.4; 156-230; 40-2