METHOD OF COATING YARN

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The present invention relates to an improved yarn of the glass fiber type and to a method of producing the improved coated yarn. A yarn formed of fiber glass, of course, is composed of a plurality, usually several hundred, individual filaments which have been drawn from a forming bushing, subsequently cooled to harden them and thereafter combined with like formed strands by twisting, using generally leaving a sound to form the ultimate composite yarn. It is conventional, of course, to treat the individual filaments and similarly it has been general practice to coat the ultimate yarn with a resin, usually a vinyl resin, to form a composite vinyl-yarn product. The coated yarns may thereafter be woven to form fabric or other weaves or constructions and generally in accordance with the particular end use for which the woven fabric will be put, e.g. yard goods, drapery material, etc. Some of the coated yarns are not close woven but are combined in an open type weave construction to yield a definitely perforate, screen-like material which is adapted to be mounted in a frame and used for window screening and the like.

Coatings for yarns of glass fiber and the like which are to be used in the last mentioned application have evidenced and demonstrated some shortcomings and drawbacks in the application thereof to the yarn and in the preparation of the screen. Thus, some yarn coatings have been found to be subject to flattening at the point of juncture of crossing yarns, e.g. those at right angles. This indicates that the coating is too soft and while a slight weld between the coating yarns is desirable it is not desirable for the coated yarn to become flattened since this leads to a weakening and ultimate breaking of the screen. Most desirably the yarn should retain the cross sectional shape in which it is finally formed in the coating operation. This cross section is usually circular with the individual filaments or strands in uniform relationships to each other and embedded in more or less of a matrix of the coating material.

It has also been found that the coatings usually formed of a vinyl resin (utilizing a vinyl plastisol technique) are not resistant to exposure to the normal temperature and atmospheric conditions. It has been suspected that the deficiency of the coatings used heretofore is due to the fact that the plasticizer component of the vinyl plastisol bleed from the yarn leaving a somewhat rigid or stiffened vinyl resin. The more rigid or stiffened vinyl matrix, of course, cannot endure any type of flex without having cracking induced therein leading to the ultimate destruction of the yarn or of the screen composed thereof.

Furthermore, the vinyl plastisol technique is quite slow, necessitating particular time/temperature relationships to effect fusion of the vinyl chloride without any heat degradation.

It is the object of the present invention to provide a novel method of coating yarn of fiber glass or the like which method overcomes the above-noted deficiencies.

It is another object of the present invention to provide a method which may be carried out very expeditiously and simply without serious or extensive modification of existing apparatus and assembly line setups.

It is still another object of the present invention to provide a coated yarn of fiber glass or the like which coated yarn is more flexible and weather resistant than yarns known heretofore in the art.

It is yet another object of the present invention to provide a method of the character described which method is flexible in that several steps can be interchanged and adjusted to meet the particular requirements of the ultimate yarn.

It is another object of the present invention to provide a method as just described which, at the same time, permits the production of a coated yarn which is more flexible, stronger and resistant to deleterious influences than heretofore known.

It is likewise an object of the present invention to provide a yarn of glass fibers or the like bearing a metallic reflective and conductive coating.

It is also an object to provide a method for producing a yarn bearing a coating which is reflective and conductive.

The above, as well as other objects of the present invention, will become apparent to those skilled in the art from the following detailed description of the invention together with specified recitation of examples of the specific and the best mode of carrying out the process of the invention to yield the novel and improved coated yarn of glass fibers or the like.

In its simplest embodiment the present invention contemplates the placing of several distinct coatings onto the yarn followed by the subjection of the coated fiber to a hot air oven to set the coatings. One of the coatings applied to the yarn constitutes an intimate physical mixture of a fusible vinyl plastisol and a polymerizable material which is either a substance containing epoxy functionality or a substance containing active isocyanato groups. The other coating comprises a relatively low boiling substance which is capable of catalyzing the polymerization of the epoxy containing substance or the isocyanato group containing substance. As indicated, the coated yarn is subsequently exposed to an environment which will cause the low boiling substance to migrate into the other coating and initiate the polymerization of cross linking of the epoxy or isocyanato group containing substance. The condition should also, of course, effect simultaneous fusion or gelation of the vinyl plastisol. Vinyl plastisol materials are, of course, well known in the art as constituting a mass of vinyl chloride polymer particles suspended in a matrix formed usually of a plasticizer. The plastisol is a fairly viscous liquid which, when heated, causes the plasticizer usually a phthalate ester or a substituted phthalate ester to permeate the vinyl chloride particle and swell it. As it swells and the temperature is elevated, a fused or gelled product is formed which is either rigid or relatively soft and flexible depending upon the proportions of the raw materials which have been combined with the vinyl chloride powder or particles. In accordance with one aspect of the present invention we modify the vinyl plastisols known heretofore, and as briefly described hereinabove, by including therein...
another polymerizable substance. One of the polymerizable substances which we incorporate as a modifying ingredient is an epoxy resin. These are known conventionally in the trade as "epoxides." The epoxides are generally hydrocarbon in nature and contain attached thereto, as a predominant functional group, the radical

\[
\text{O} \quad \text{C} \quad \text{O} \quad \text{CH} \quad \text{CH} \quad \text{O} \quad \text{C} \quad \text{O} \quad \text{C} \quad \text{O} \quad \text{CH} \quad \text{CH} \quad \text{O} \quad \text{C} \quad \text{O} \quad \text{C} \quad \text{O} \quad \text{C} \quad \text{O}
\]

The epoxide, diepoxide or polypoxide (containing one or more

\[
\text{O} \quad \text{C} \quad \text{O} \quad \text{CH} \quad \text{CH} \quad \text{O} \quad \text{C} \quad \text{O} \quad \text{C} \quad \text{O} \quad \text{C} \quad \text{O} \quad \text{C} \quad \text{O} \quad \text{C} \quad \text{O} \quad \text{C} \quad \text{O} \quad \text{C} \quad \text{O}
\]

groups) may be a relatively simple monomer or it may be derived from a somewhat longer chain complex ester or carbocyclic acid function replaced by the epoxy group or the epoxide radical. The epoxide group polymerizes by a breaking or schism of one of the carbon oxygen bonds leading to the formation of ether linkages in the polymerize. Also epoxy groups may cross link with epoxy groups in an adjacent chain. Most preferably, the epoxide for use in the present invention should be an epoxide which has a degree of flexibility already built into the backbone of the polymer. An example of such an epoxide is ethylene glycol diepoxide having the structural formula:

\[
\text{O} \quad \text{C} \quad \text{O} \quad \text{CH} \quad \text{CH} \quad \text{O} \quad \text{C} \quad \text{O} \quad \text{C} \quad \text{O} \quad \text{C} \quad \text{O} \quad \text{C} \quad \text{O}
\]

where \( x \) varies from 2 to about 10. Another group of compounds having inherent flexibility is the modified triglycerides. Such materials are illustrated, for example, by epoxydized soybean oil or epoxidized tall oil. In such cases oxidation of the \( \text{CH}_2 \text{CH} \text{O} \) non-conjugated olefinic fatty acid yields the epoxidized ester. The epoxy group may also be present on the benzene ring portion of a phthalic ester in which the ester portion is a long chain fatty acid derivative.

The epoxide is combined with the vinyl plastisol by simply mixing the two ingredients together with a conventional plasticizer such as one or more of the alkyl substituted phosphates or one or more of alkyl substituted halate esters, or mixtures thereof. The epoxide and the conventional vinyl plasticizer should be combined in such amounts as to constitute a total of from about 35 to about 65 parts of these two components per 100 parts of dry vinyl chloride. Preferably the vinyl plastisol, as so modified ready to be applied to the yarn, should have a viscosity between about 2,000 centipoises and about 10,000 centipoises. A plastisol within this range is quite practically workable,insuring efficient and uniform distribution of the epoxide throughout the plastisol and at the same time providing effective coating of the yarn together with impregnation of the free spaces or interstitial voids between the plurality of filaments.

The fusible vinyl chloride plastisol may also be modified, in accordance with the invention, by including therein, to form an intimate physical mixture, an amount of a substance containing reactive isocyanato groups or a substance which is capable of yielding isocyanato reactive groups under the conditions of the coating or under the oven drying conditions subsequent thereto. Materials containing active isocyanato groups are, for example, the organic disiocyanates including ethylene disiocyanate; trimethylene disiocyanate; tetramethylene disiocyanate; hexamethylene disiocyanate; decamethylene disiocyanate; m-phenylene disiocyanate, p-p-diphenyl disiocyanate, napththalene disiocyanate and like compounds. When the added ingredient is an isocyanate or disiocyanate having active \(- \text{N} = \text{C} = \text{O}\) groups, there should, preferably, be included a copolymerizing substance having reactive hydrogen groups such as a polyester or a polyurethane glycol. It is not always necessary, of course, to use a copolymerizing substance since the diisocyanates will copolymerize in and of themselves. Frequently, it is desirable to use an isocyanate which has been previously reacted to form an adduct thereof. Thus, particularly in the case of disiocyanates, an adduct of the disiocyanate with a hydroxyl containing, alkyl, alkenyl, aralkyl or like compound is desirable since the aryl radical blocks the reactivity of the isocyanate group. A mixture of vinyl plastisol and an adduct of, for example, ethylene disiocyanate and phenol possesses improved shelf life. The adduct of phenol will be found, upon exposure to the elevated temperature in the drying oven as described hereinafter, to have given up the phenol group revealing the reactive isocyanato group for rapid polymerizing at the desired time.

Preferably, in accordance with this invention the presence of water in the plastisol or during the coating operation should be avoided since the conventional ester isocyanate tends to react preferentially therewith reducing the copolymerization of the \(- \text{N} = \text{C} = \text{O}\) with the hydroxyl containing polyester, polyykylene ether glycol or the like and thereby detracting from hardness, toughness and the like. In combining the isocyanate and the reactive hydrogen containing compound with the vinyl plastisol, the isocyanate should be present in sufficient amount that there are present therein an excess of NCO groups in order that in the final oven curing step the isocyanate may react with the urea or urethane groups to provide a branching of the intermediate linear chains or the cross linking of already formed branch chains.

The polyester adducts are known in the art and no detailed description need be given beyond stating that they are formed from the condensation products of dicarboxylic acids and dihydric alcohols. The polyykylene ether glycols are also known in the art to constitute condensation products of alkylene oxides capped, for example, at a terminal stage of the reaction with, for example ethylene oxide to stop the reaction and prevent it from continuing to an undesirable high molecular weight. The polyykylene glycols or ether glycols may also be condensed with polyhydric materials to yield more reactive substances for forming various adducts with the isocyanate or polyisocyanate. The use of polyhydric materials such as pentacyrthritol (containing a large proportion of primary hydroxyl groups) tends to result in a greater amount of hardening of the ultimate isocyanate or a urethane reaction product concurrent with the fusion of the vinyl plastisol.

The combination or modification of the vinyl plastisol with the isocyanato group containing substance, or adduct of such isocyanato substance, should follow the same general procedure as set forth hereinafore in the description of the combination of the vinyl plastisol and the epoxy additive. That is, the combination will usually include an amount of a conventional type plasticizer. The relative amount of the isocyanato or isocyanato adduct and the conventional vinyl plasticizer should be selected as to constitute a total of from about 35 parts to about 65 parts of these two components per 100 parts of dry vinyl chloride, calculated on a dry basis.

It has been found that when the isocyanato containing substance or adduct with the reactive hydrogen containing compound does not function as a plasticizer to the extent that the epoxide modifier does. Accordingly, in the case of the latter, the epoxide may constitute the major proportion of the plasticizer, e.g. as much as 45 parts epoxide to 20 parts vinyl plastisol (total of 65) to 100 parts of vinyl chloride. In the case of the isocyanato group containing substance the conventional plasticizer should be at least equal to the amount thereof, e.g. about 32 parts of isocyanato group containing sub-
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stance to 32 parts plasticizer to 100 parts of vinyl chloride. This is particularly true in the case of the use of the polyyurethane adduct of the diisocyanate and a poly-
ether glycol containing an appreciable proportion of primary hydroxy containing monomers such as pentae-
rythritol, trimethyl propane or the like. On the other hand, with the more flexible polymer containing less of the polyhydroxy monomers the amount of the urethane may be greater, approaching 40–50 parts per 100 parts of the vinyl chloride. In any event, the amount of the urethane or isocyanate group containing substance should not be such as to affect materially the viscosity of the vinyl plastisol since if the viscosity must be such that it can be expeditiously applied to the yarn of glass fibers and the like and, at the same time, urged into the interstices, spaces or voids between the individual filaments making up the yarn.

The other coating for the production of yarn in accordance with the present invention is composed, for example, of a catalyst capable of polymerizing the additive added to the vinyl plastisol. The coating may be formed of a dispersion of the catalyst per se in a vinyl plastisol or in a suitable carrier. Broadly speaking, the catalyst should be one which is capable of catalyzing the epoxy polymerization and may be also capable of initiating the epoxy ingredient or capable of polymerizing the NCO or isocyanate group containing substance. A catalyst for one, of course, is not always a catalyst for the other. Accordingly, the invention contemplates the employment of catalyst for the epoxy group where the epoxies are utilized as the additive for the vinyl plastisol and it en-
visions the employment in one coating of a catalyst of the isocyanate group, an isocyanate adduct or urethane where the latter is employed as the additive for the vinyl plastisol.

Amines including primary, secondary and tertiary amines and diamines represent one group of organic cata-
ylists which are capable of catalyzing both the epoxy polymerization and the polymerization of compounds containing active or free NCO groups. The tertiary amines, of course, are particularly effective catalysts of the polymerization of cross linking of —NCO containing compounds. Examples of amines are diethylamline, permethylated diethylene triamine, triethylene tetramine, hexahydrodimethyl aniline, alkyl morpholines, etc. The aliphatic diamines are in general more reactive than the aromatic diamines. Furthermore, they have lower boiling points and are therefore preferred. Examples are: diamino propyl diethylene triamine; triethylenetriamine; trifururylamine; diethylene triamine; polyethylene glycol diamine; diisoproplamine; diisobutylamine; tripropyla-
mine; 2-ethyl butyl amine; 2,2-dimethyl butyl amine; sym-
metrical triazine; alkyl and/or aryl substituted piperezine, the latter compound Piperazine having the formula:

\[
\begin{array}{c}
\text{N} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{N} \\
\text{H} \\
\end{array}
\]

and the like. The gaseous amines on the other hand, that is those having boiling points below room tempera-
ture, are not desirable since they are not retained in the vinyl plastisol but rather escape before they can be effec-
tively coated onto the yarn or overcoated with the second coating of vinyl plastisol followed by an introduction into the curing oven. On the other hand, even the gaseous amines may be used if they are ones which are soluble in the plastisol or in any solvent or other ingredient in-
cluded with the vinyl plastisol.

Carbamate acid esters are also catalysts for the iso-
cyanato group. These are obtained by reacting an aliph-
atic or aromatic or a monohydroxy or polyhydroxy compound with a monoisonocyanate. The hydroxy com-
 pound may be methyl, or ethyl, or propyl or butyl or higher aliphatic alcohol or cyclohexanol. In addition, benzyl alcohol is permitted or containing less of the polyhydroxy monomers the amount of the urethane may be greater, approaching 40–50 parts per 100 parts of the vinyl chloride. In any event, the amount of the urethane or isocyanate group containing substance should not be such as to affect materially the viscosity of the vinyl plastisol since if the viscosity must be such that it can be expeditiously applied to the yarn of glass fibers and the like and, at the same time, urged into the interstices, spaces or voids between the individual filaments making up the yarn.

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\[
\begin{array}{c}
\text{N} \\
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\text{H} \\
\text{N} \\
\text{H} \\
\end{array}
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cluded with the vinyl plastisol.
solvent, such as xylene, toluene or the like. In addition to being capable of catalyzing the epoxide or NCO-containing additive to the vinyl plastisol, the catalyst must be relatively low boiling and also, preferably, it should be soluble or diffusible into the coating composed of the vinyl plastisol and the additive, e.g. the epoxide.

The coatings may be applied to the yarn in any sequence. Thus, the catalyst or catalyst containing coating may be applied first, followed by the application of the coating composed of the vinyl plastisol and resinous additive. Conversely, the coating of the vinyl plastisol and resinous additive may be applied first, followed by the application of the catalyst or catalyst containing coating.

The latter, in addition, of course, to being applied per se or in a carrier or diluent, may be formed in or supplied in the vinyl plastisol. In such cases, it is a simple matter to adjust the amount of vinyl plastisol in the several coatings to provide the amount desired, as in the case where the vinyl plastisol is present in just one of the coatings. Where the catalyst or catalyst containing coating is to be applied first, it is sometimes desirable to preheat the yarn of glass fiber in order to provide an initial driving force for the catalyst migration into the subsequently applied coating of vinyl plastisol and resinous additive.

It is frequently most desirable to carry out the sequence of coatings such that the catalyst or catalyst containing coating is applied first, followed by the coating of plastisol containing the resinous additive (the epoxide, isocyanato group containing compound or adduct capable of undergoing cross linking polymerization). Such a sequence provides polymerization from a point nearest the glass surface proceeding therefrom outwardly, as it were. This avoids and/or reduces the formation of any blistering, such as may occur in a rigorous cross linking reaction of the resinous additive. Furthermore, it avoids and/or reduces the formation of any skin on the outer surface of the coated yarn.

In accordance with another aspect of the present invention, the amount of catalyst may be selected so as to be insufficient to cause polymerization of all of the epoxide, C-9.

The advantage of this procedure is that the resulting final plastisol coating will be inherently stable against heat degradation, such that exposure to heat will first completely polymerize before being able to exert any heat degradation influence on the plastisol coating.

The coatings are applied conventionally, that is, the coatings are applied by simply allowing a stream of the liquid catalyst or viscous resin to flow onto the laterally moving yarn. The yarn immediately moves laterally through a wiping die which has an orifice which is flared slightly to meet the incoming strand and, by reason of the size of the orifice of the die, to adjust the amount of coating adhering to the strand or yarn as it passes there beyond. The yarn, of course, is unwound from a conventional reel containing a continuous length of the yarn. After the first coating is applied to the yarn, it passes immediately in continuous fashion through a falling stream of the second coating and thence to a wiping die. This wiping die also possesses an orifice to adjust the amount of the second coating onto the previously coated yarn. After passing through the second wiping die, the yarn proceeds laterally into a hot air oven which is maintained at atmospheric pressure. The temperature in the curing oven is maintained at about 450° F. in order to effect fusion or gelation of the vinyl plastisol. The oven is of a size to permit gelation considering the temperature noted and the amount of resin which has been put onto the yarn. All of these factors are well known in the art and need not be described or illustrated beyond the just preceding description, since the application of the principles and spirit of the present invention can be readily incorporated into the commercially used operations by those skilled in the art.

Polyester resins may also be used to form a polymerized resinous network within the vinyl plastisol coating in place of epoxides of isocyanato group containing compounds. Polyester resins are, generally speaking, condensation products of polyfunctional acids and polyfunctional alcohols and sometimes including fatty acid and/or fatty acid containing drying oils. They are heat and catalyst convertible to an infusible mass. Catalysts for the polyester resin additive to the plastisol are of the free radical type and include the peroxy catalysts, such as benzoyl and lauryl peroxide; organometals, such as triethyl aluminum, zinc naphthenate, etc. and others well known in the art. Since these are for the most part solid materials, they are usually desirably included together with the polyester in the vinyl plastisol and the coating accomplished in one step. Care must be exercised, however, to prevent premature catalysis and polymerization of the polyester prior to fusion of the plastisol, i.e., before the resin is polymerized.

Liquids catalysts for polyester resins, on the other hand, particularly if capable of boiling below 450° F., can be used as a separate coating component permitting a greater flexibility of operation, whereby the catalyst will migrate or diffuse into the polyester containing plastisol coating layer to polymerize the polyester and yield a stronger, tougher coating.

It is frequently desirable to apply a size prior to the application of the catalyst or resinous additive (epoxide, isocyanato group containing compound) containing plastisol. In such case, we prefer to utilize a more or less conventional starch or gelatin size but modified to contain a very small amount of a Werner chromium complex, such as stearato-chromyl chloride and related water-soluble, coordinated compounds wherein the acid group has less than 10 carbon atoms. This pre-sizing repels any water or moisture and prevents and/or reduces any tendency of the after-applied coatings being attacked at the interface of the glass fiber and said coating.

In accordance with another embodiment of the present invention, we apply a first coating of a vinyl plastisol and resin onto a yarn composed of glass fibers (using either a wiping die or by passing the yarn over a rotating drum which picks up the coating and another drum partially immersed in a tank of the coating) and thereafter the coated yarn is passed through a special wiping die, which is essentially a hollow annular ring having spaced ports facing radially inward toward the orifice. This hollow annular ring is fluid-connected to a supply of catalyst for the resin and the connection includes a metering pump which permits the catalyst to be directed to the ports in any pre-selected quantities depending upon the character of the resin used. The catalyst is thus forced into the plastisol coating and together with the wiping action of the die, e.g., the contact of the orifice with the plastisol, serves to vigorously mix the catalyst completely therethrough, whereby the plastisol is polymerized rapidly and contemporaneously with fusion of plastisol. The operation proceeds most efficiently, particularly where a 'hot' catalyst is employed.

While there should be no limitation inferred from the following theoretical explanation, it is believed that the efficacious results achieved by the present invention are obtained in the following manner. The additive resinous material, e.g. the epoxy group containing material or the isocyanato adduct thereof or urethane, are intimately mixed with the particles of vinyl chloride which are floating, as it were, in the plastisol. Where the plastizer content is relatively high, the particles (particularly when the temperature is raised) commence to swell, bringing the particles into surface to surface contact. The low boiling character of the preferred additive in
accordance with this invention permits the additive to penetrate along with the plasticizer into the actual particle. The catalysis due to the subsequent coating containing the catalyst for the additive effects cross linking or polymerization to form, as it were, a reinforcing network chain within the vinyl chloride monomer as it continues to swell and fuses finally in the heating step within the hot air oven. In the case of a rather low plasticizer content vinyl plastisol, the vinyl chloride particle nonetheless swells to some degree and the additive resin, e.g. the epoxy or the NCO or the NCO adduct or the urethane, surround the individual particles floating in the plasticizer matrix. The applied catalyst is in the second coating polymerizes the resinous phase, there is again formed a network or chain throughout the simultaneously fused vinyl chloride plastisol layer furnishing a reinforcement of the plastisol coating. It is further believed that this network, whether it be formed one way or the other as described hereinabove, serves to provide a barrier against loss of plasticizer upon exposure to otherwise deleterious influences in the final application. Thus, high temperature, sun, water, and general weathering conditions, which would normally cause the plasticizer component to leach or become leached out of the coating, are prevented from so doing by the presence of the separate resinous phase which is of stronger character than the fused vinyl chloride polymer itself.

There will now be described several preferred formulations and methods for carrying out the practice of the present invention in accordance with the explanation given in detail hereinabove.

**EXAMPLE I**

A mixture of vinyl chloride polymer plastisol and epoxide resin is prepared in accordance with the formulation of Table 1 below.

**Table 1**

<table>
<thead>
<tr>
<th>Material:</th>
<th>Weight, amt. in grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vinyl chloride resin (Monsanto—Opalon 410)</td>
<td>1200</td>
</tr>
<tr>
<td>Phthalate and phosphate plasticizers</td>
<td>350</td>
</tr>
<tr>
<td>Aluminum paste colorant</td>
<td>12</td>
</tr>
<tr>
<td>Barium and cadmium stearates</td>
<td>36</td>
</tr>
<tr>
<td>Hydrocarbon solvent diluent</td>
<td>89</td>
</tr>
<tr>
<td>Ethylene glycol diepoxide</td>
<td>206</td>
</tr>
</tbody>
</table>

The foregoing ingredients were charged to a container and stirred to insure a complete and intimate dispersion of the ingredients. It was then set aside for the moment and there was prepared a second mixture of ingredients according to the formulation of Table 2.

**Table 2**

<table>
<thead>
<tr>
<th>Material:</th>
<th>Weight, amt. in grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vinyl chloride resin (Monsanto—Opalon 410)</td>
<td>1200</td>
</tr>
<tr>
<td>Phthalate and phosphate plasticizers</td>
<td>200</td>
</tr>
<tr>
<td>Aluminum paste colorant</td>
<td>12</td>
</tr>
<tr>
<td>Di-N-dioctyl adipate</td>
<td>132</td>
</tr>
<tr>
<td>Filler</td>
<td>48</td>
</tr>
<tr>
<td>Stabilizer</td>
<td>36</td>
</tr>
<tr>
<td>Epoxidized soybean oil</td>
<td>268</td>
</tr>
<tr>
<td>Diamyl propyl diethylene triamine</td>
<td>86</td>
</tr>
</tbody>
</table>

The above ingredients were mixed thoroughly and set aside for use in the practice of the invention. Next, from an annular reel containing a continuous supply of yarn of assembled and twisted glass fibers, there was drawn in continuous fashion a strand of the plastic fibers which was passed through two wiping dies arranged in spaced-apart series relationship and thence through a drying oven and finally to a wind-up reel. The openings in the respective wiping dies were adjusted so as to apply, as determined by trial and error, an amount of a final coating onto the yarn such that it constituted 50% of the total weight of the dried coated yarn. The coating of ingredients, set forth in Table 1 above, was poured as a narrow stream onto the continuously traveling yarn. The mixture of ingredients, set forth in Table 2, was applied subsequently at the second wiping die. The doubly coated yarn then passed into the drying oven where the temperature was maintained at 450° F. The yarn proceeding from the drying oven possessed a coating which was dry and strong. It completely encapsulated the individual filaments making up the yarn.

The mixtures, just described, possess a viscosity of about 4,000 centipoises. The final composite coating was dry and tough to the fingernail. The coated yarn was very nicely to give a screen which did not soften at the point of the juncture of coating yarns; the point of crossing was not flattened, although the crossing varas were well cohered together.

**EXAMPLE II**

Mixtures of ingredients as described in the preceding example were prepared. The yarn was passed as described previously through two spaced-apart wiping dies in series and thence through a drying oven maintained at about 450° F. The mixtures, however, were applied in reverse order to that described in the previous example. That is, the mixture according to the formulation in Table 2 was applied to the yarn first via the first wiping die, followed by the application of the mixture according to the formulation in Table 1 through the second wiping die. In this fashion the catalyst-containing coating was applied first. This catalyst-containing coating polymerized and/or linked the diepoxide as principally the outer layer of the two-layer assembly. This created a harder reinforced phase at the outer portion of the coated strand. The ultimately coated yarn was again found to be tough when scratched with a fingernail, and was woven successfully into a screen-type material. The crossing yarns of the woven material cohered well together, yet did not flatten out, e.g. they retained their circular cross-sectional contour.

**EXAMPLE III**

The procedure of the preceding example was repeated except that prior to the application of the first coating (catalyst containing) through the wiping die, the yarn of assembled glass fibers is preheated to a temperature of about 400° F. The remainder of the procedure was exactly the same. This procedure, where the yarn is preheated, has the effect of accelerating the diffusion of the amine catalyst component throughout the two coatings whereby the yarn can be drawn through the wiping dies or coating operation and the drying oven at a faster rate than heretofore, e.g. 800 ft. per minute. The normal speed at which the yarn travels is 450 ft. per minute.

**EXAMPLE IV**

A plastisol coating was prepared in accordance with the formulation, set forth in Table 3.

**Table 3**

<table>
<thead>
<tr>
<th>Material:</th>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vinyl chloride (Monsanto—Opalon 410)</td>
<td>10</td>
</tr>
<tr>
<td>Plasticizer</td>
<td>3.05</td>
</tr>
<tr>
<td>Epoxidized soybean oil</td>
<td>1.9</td>
</tr>
<tr>
<td>Colorant paste</td>
<td>.6</td>
</tr>
<tr>
<td>Stabilizers</td>
<td>.35</td>
</tr>
<tr>
<td>Hydrocarbon solvent diluent</td>
<td>.7</td>
</tr>
</tbody>
</table>

The above ingredients were mixed by adding the vinyl chloride to the container in which had been introduced the plasticizer components. The other ingredients were added subsequently and stirred to produce a somewhat viscous sirup having a viscosity in the neighborhood of 5,000 centipoises. This mixture was set aside while the
following mixture was prepared in accordance with the following formulation:

<table>
<thead>
<tr>
<th>Material</th>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vinyl chloride resin (Monsanto—Opalon 410)</td>
<td>10</td>
</tr>
<tr>
<td>Plasticizer</td>
<td>4.95</td>
</tr>
<tr>
<td>Colorant paste</td>
<td>0.6</td>
</tr>
<tr>
<td>Stabilizers</td>
<td>0.35</td>
</tr>
<tr>
<td>Hydrocarbon diluent</td>
<td>0.7</td>
</tr>
<tr>
<td>Polyethylene glycol diamine</td>
<td>0.6</td>
</tr>
</tbody>
</table>

The above ingredients were mixed in the same manner as the just previously mentioned mixture. These mixtures were applied in turn to a continuously moving yarn composed of glass filaments, passed between wiping dles to adjust the amount of coating adhering and thence passed through a drying oven maintained at 450° F. The double coated yarn was then wound up on a reel continuously. Examination revealed the yarn to be uniformly coated and said coating to be tough when scratched with the fingernail. A similar procedure, employing only the coating mixture of Table 3 above, was found to yield a coated yarn which by comparison was softer and otherwise less desirable than the yarn bearing the two coatings. The second coating (according to Table 4) containing the polyethylene glycol diamine and the epoxy group component of the first mixture making it tougher and harder. Furthermore, exposure of the double coated yarn to temperature and weathering conditions, which would normally cause the coating to become more brittle, did not affect the double coated yarn in accordance with the present example.

**EXAMPLE V**

The mixtures described in Example IV were applied in this example as coatings but in reverse order, namely, the catalyst-containing mixture containing the polyethylene glycol diamine was first applied, followed by the mixture containing the epoxidized soybean oil. The conditions were otherwise the same. The resultant coated yarn was tough and scratch resistant. Close examination revealed it to constitute about 50% coating and 50% yarn. The coated yarn was easily woven into an open weave construction, yielding a very desirable screening material. The point of juncture of the crossing yarns did not evidence any flattening. Rather, the yarns were circular in cross section at the point of crossing, thereby having improved ultimate strength.

**EXAMPLE VI**

To illustrate the use of a urethane containing vinyl plastisol there was prepared as a first mixture the ingredients, set forth in Table 5.

<table>
<thead>
<tr>
<th>Material</th>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vinyl chloride (Monsanto—Opalon 410)</td>
<td>10</td>
</tr>
<tr>
<td>Mixture of plasticizers</td>
<td>4.95</td>
</tr>
<tr>
<td>Stabilizers</td>
<td>0.35</td>
</tr>
<tr>
<td>Colorant paste</td>
<td>0.2</td>
</tr>
<tr>
<td>Antimony oxide Sb2O3</td>
<td>0.4</td>
</tr>
<tr>
<td>Hydrocarbon solvent diluent</td>
<td>0.5</td>
</tr>
<tr>
<td>Urethane adduct</td>
<td>0.80</td>
</tr>
</tbody>
</table>

The above identified urethane adduct is a reaction product of tolylene diisocyanate, polyester and phenol. The above ingredients are mixed in the usual fashion, adding the urethane adduct near the end. The mixture has a viscosity in the neighborhood of 3,000 centipoises and is easily applied to a continuously moving yarn of glass fibers in the usual fashion. As a second coating there is applied a somewhat viscous alcohol solution of dimino propyl diethylene triamine. This solution was somewhat thinner than the plastisol mixture given in the table just above. However, it is applied conveniently and in the passage of the coated yarn through the drying oven, maintained at 425° F., the amine catalyst diffuses or permeates the first vinyl plastisol coating and effectually initiates cross linking of the ethylenediamine adduct, yielding an ultimately coated yarn which is tougher and more weather resistant than heretofore conventional yarns coated with vinyl plastisol alone.

In accordance with another aspect of the present invention, it is desired to apply a reflective and conductive metallic coating on a plastic coated yarn in order to provide tarnish resistance and, in addition, yield a yarn which is extremely eye pleasing due to the reflective coating and is capable of transmitting heat and/or electricity for many applications where such properties would be advantageous. To accomplish the foregoing most expeditiously, there is prepared a plastic coating mixture such as a vinyl plastisol in a manner well known in the art. To this there is added a reducing agent compatible with the vinyl plastisol. Examples are: hydrazine, the hydrides of lithium, sodium, potassium, etc., the hydrosulfite salts of these same metals, and other strong reducing agents. The so formed liquid reducing agent-containing coating is applied to the yarn of glass fibers by passing it through a bath thereof or about a pick-up drum. Next, the coated yarn is passed through another bath or in contact with a pick-up drum where a solution of a silver, copper or gold salt is applied to the previously coated yarn. Typical salts is silver nitrate, phosphates, carbonates, sulfonates, and the like. As indicated, the salts of silver, copper and gold are preferred; however, other salts of metals above hydrogen in the Electromotive Series of metals are useful. These include arsine, antimony, bismuth, mercury and platinum.

While we have disclosed, hereinabove, certain preferred modes of performing our invention, we do not thereby desire or intend to limit ourselves solely thereto; furthermore, the proportions of the materials utilized may be varied and equivalent chemical materials may be employed, if desired, while departing from the spirit and scope of the invention as defined in the appended claims.

We claim:

1. The method of coating a glass fiber yarn as to adapt it for use as a perforate screen defining element, said method comprising: (1) applying to the yarn a coating comprising a low boiling substance capable of catalyzing polymerization of a material selected from the group consisting of an epoxy containing substance and an isocyanato group containing substance, said substance having a boiling point above room temperature but not greater than 450° F. (2) applying a second coating of a flowable composition comprising an intimate physical mixture of a fusible vinyl plastisol and a polymerizable material selected from the group consisting of epoxy containing substances and an isocyanato group containing substance and (3) exposing said coated yarn to a temperature sufficient to cause said substance to migrate into said second coating layer and polymerize said polymerizable and sufficient to simultaneously fuse said plastisol whereby the presence of said polymerized material reduces plasticizer loss normally associated with exposure of the coated yarn to elevated temperature and weather conditions.

2. The method of coating a glass fiber yarn as to adapt it for use as a perforate screen defining element, said method comprising: (1) applying to the yarn a coating comprising a relatively low boiling substance capable of catalyzing polymerization of an epoxy containing substance, said substance having a boiling point above room temperature but not greater than 450° F. (2) applying a second coating of a flowable composition comprising an intimate physical mixture of a fusible vinyl plastisol and an epoxy containing substance and (3) exposing said coated yarn to a temperature of from 300° F. to 450° F. to cause said low boiling substance to migrate into said second coating layer and polymerize said epoxy and suffi-
cient to simultaneously fuse said plastisol, whereby the presence of said polymerized material reduces plasticizer loss normally associated with exposure of the coated yarn to elevated temperature and weather conditions.

3. The method of coating a glass fiber yarn as to adapt it for use as a perforate screen defining element, said method comprising: (1) applying to the yarn a coating of a relatively low boiling substance capable of catalyzing polymerization of an isocyanate group containing substance, said substance having a boiling point above room temperature but not greater than 450° F. (2) applying a second coating of a flowable composition comprising an intimate physical mixture of a fusible vinyl plastisol and an isocyanate group containing substance and (3) exposing said coated strand to a temperature in the range of 300° F. to 450° F. to cause said low boiling substance to migrate into said second coating layer and effect polymerization of said isocyanate group and sufficient to simultaneously fuse said plastisol, whereby the presence of said polymerized material reduces plasticizer loss normally associated with exposure of the coated yarn to elevated temperature and weather conditions.

4. The method of coating a glass fiber yarn as to adapt it for use as a perforate screen defining element, said method comprising: (1) applying to the yarn a coating of a liquid composition comprising an intimate physical mixture of a fusible vinyl plastisol and a polymerizable material selected from the group consisting of epoxy containing substances and an isocyanate group containing substance (2) applying a coating of a relatively low boiling substance capable of catalyzing polymerization of a material selected from the group consisting of epoxy containing substances and an isocyanate group containing said low boiling substance having a boiling point above room temperature but not greater than 450° F. and (3) exposing said coated strand to a temperature causing said low boiling substance to migrate into said first coating layer and polymerize said polymerizable material and sufficient to simultaneously gel said plastisol to thereby yield a strand bearing a coating which is strong and resistant to weathering, by reason of the presence of the stronger polymerize throughout the fused vinyl plastisol coating.

5. The method of coating a yarn as claimed in claim 1 wherein the yarn is preheated prior to step 1.

6. The method as claimed in claim 4 wherein the coating of step 1 possesses a viscosity of from 2,000 to 10,000 centipoises.

7. The method as claimed in claim 2 wherein the amount of catalyst is selected to be insufficient to cause polymerization of all of the epoxy groups whereby the resulting coated yarn is stabilized against heat degradation.

8. The method as claimed in claim 1 wherein the coating of the first step comprises in addition a vinyl plastisol component.

9. The method as claimed in claim 1 wherein the substance of step 1 has the formula $Y Si(OR)_n$ where R is a lower alkyl group, Y is an amine and a and b are positive numbers whose sum is 4.

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