

1

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**PROCESS FOR SIZING GLASS FILAMENTS AND PRODUCT PRODUCED THEREBY**

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This invention relates to a process for producing glass filaments wherein said filaments are treated with a sizing material. More particularly, this invention relates to the process of treating glass filaments with a sizing material comprising the condensation product of a difunctional halohydrin with an aliphatic amine. Still further, this invention relates to a process for treating glass filaments with a sizing material comprising the condensation product of epichlorohydrin with an aliphatic amine containing at least 16 carbon atoms. Still further, this invention relates to the products produced in accordance with the process of the present invention.

One of the objects of the present invention is to size glass filaments with a sizing material comprising the condensation product of a difunctional halohydrin with an aliphatic amine. A further object of the present invention is to apply the sizing material to the glass filaments by spraying the sizing material onto said filaments. A still further object of the present invention is to apply the sizing material to the glass filaments by passing said filaments through an aqueous bath of the sizing material. These and other objects of the present invention will be discussed more fully hereinbelow.

The process for the preparation of the glass filaments to be treated in accordance with the present invention are well known in the art, as represented by U. S. Patents 2,133,236, 2,133,238 and 2,175,225 amongst others. These filaments are generally of extremely small diameter, in the order of magnitude of about 0.0002-0.0004 inch, and are combined into a strand containing generally about 200-204 or more filaments. These glass filaments have exceedingly high tensile strength and find application in a great many fields. These filaments, however, are combined in great plurality to form strands wherein one filament is in close contact with adjacent filaments. If these filaments are to be combined into a single strand, without benefit of any protective covering on the filaments, the individual filaments tend to rub against one another, which causes a breakdown of the individual filaments and ultimately a breakdown in the entire strand, due to attrition. It is, then, desired to apply a sizing material to these individual filaments, so that when combined into a strand, they will be sufficiently protected so as to avoid loss due to attrition. In the manufacture of these glass filaments, molten glass maintained at a temperature of about 2500° F. is allowed to pass through a great plurality of dies in the base of the furnace to form glass threads or filaments which are drawn downwardly at about 6,000-10,000 feet per minute. Almost immediately after the filaments are drawn down from the dies, it is desired to apply a sizing coating to the individual filaments in order to protect them from loss due to attrition. The size coating is applied to individual filaments while the filaments are still in a comparatively hot condition. These filaments are then gathered to form a strand and are subsequently heated so as to drive off the aqueous vehicle, thereby developing the sizing properties of the condensation product while in direct contact with the filament. The manner of application of the sizing material to the filaments can be varied very considerably. The individual filaments may be sprayed with the sizing material while the filaments are still hot, or the individual filaments may be passed at least partially around a sizing applicator roll, wherein the filaments will become coated with the sizing material; or the filaments may be passed through an aqueous bath of the

2

sizing material, in which case the filaments are passed through the sizing bath at a high rate of speed.

In the practice of the process of the present invention, aliphatic monoamines having hydrocarbon chain lengths of 16 or more carbon atoms are reacted with a difunctional halohydrin, such as epichlorohydrin, in a quantity sufficient to form products containing from about 1-2 mols of the halohydrin condensed with each mol of the amine. The resultant condensation products are water soluble or at least water-dispersible. In the place of the aliphatic amine, one may use an aliphatic amine salt in coreaction with the halohydrin to form the condensation product. When the amine salts are used, the molal ratio of the epichlorohydrin can be considerably higher, extending up to about 3:1. This difference appears to result from the fact that the amine salts do not react with the epichlorohydrin or other halohydrins as readily or as completely as do the free amines themselves; therefore, a larger proportion of the halohydrin may be used. The fact appears to be that no more than 2 mols of the epichlorohydrin can be reacted with 1 mol of a higher aliphatic monoamine, such as octadecyl amine, regardless of the excess of the epichlorohydrin in the reaction mixture.

In general, therefore, the condensation products suitable for use in practicing the invention are those which contain from 1-2 mols of a halohydrin condensed with 1 mol of a higher aliphatic monoamine or monoamine mixture having an average molecular weight corresponding to a hydrocarbon chain length from about 16-22 carbon atoms. The preferred aliphatic monoamines are those of about 16-18 carbon atoms, since these are obtainable commercially at reasonably low cost. It will be understood that either alkyl amines (i. e., amines of saturated character) or alkenyl amines (unsaturated amines) may be employed; however, it is preferred that at least 50% of the amine hydrocarbon be fully saturated.

In preparing the condensation products, the amine is preferably dissolved in a solvent such as ethanol, propanol, butanol or the like and the epichlorohydrin is added slowly at temperatures below about 90° C. After all the epichlorohydrin has been added, the solution is heated until a water-soluble or water-dispersible condensation product is formed. The solvent can then be removed by distillation at reduced pressure and the sizing agent obtained as a waxy material. In carrying out the condensation, care should be taken to use relatively mild reaction conditions, such as temperatures not substantially higher than 100° C., and to stop the reaction when an initial condensation product has been formed. If the reaction is carried out for too long a time, or if excessively high temperatures are used, there is danger of forming a polymerized condensation product that has greatly reduced efficiency as a sizing agent and that is not readily dispersed in water. In order that the present invention may be more completely understood, the following examples are set forth, which illustrate the method for the preparation of the condensation products which are used to size the filaments. It must be remembered that these examples are set forth solely for the purpose of illustration and any specific enumeration of detail should not be interpreted as a limitation on the case except as indicated in the appended claims. All parts are parts by weight.

**CONDENSATION PRODUCT A**

A solution of 103.7 parts (0.371 mol) of "Armeen D," a commercial octadecyl amine having a molecular weight of 279.5, in 150 parts of ethanol is converted into the hydrochloride by adding 13.7 parts (0.371 mol) of concentrated hydrochloric acid. The solution was heated to 70° C. and 68.6 parts (0.742 mol) of epichlorohydrin was added at the rate of about 5-8 parts per minute while cooling sufficiently to maintain the temperature below 70° C. The mixture was then boiled under a reflux condenser for about 4 hours, the solvent removed by distillation and the product stripped under a partial vacuum. The residue is an opaque, dark brown soft wax containing 1.3 mols of combined epichlorohydrin for each mol of amine.

### CONDENSATION PRODUCT B

Solution containing 146 parts (0.5 mol) of commercial octadecyl amine in 150 parts of ethanol is prepared and heated to 65° C. To this solution, 92.5 parts (1 mol) of epichlorohydrin is added uniformly and gradually during about 12 minutes, the temperature being maintained below 75° C. The resulting mixture was boiled 4 hours under a reflux condenser, the solvent removed by distillation at reduced pressure and the residue stripped of volatiles in the usual manner. There was obtained 223.2 parts of octadecyl amine-epichlorohydrin condensation product, as a light, brittle, tan-colored wax.

### CONDENSATION PRODUCT C

A solution of 292 parts (1 mol) of commercial octadecyl amine in 300 parts of ethanol is prepared and 232 parts (2.5 mols) of epichlorohydrin are added over a 48 minute period. The mixture was refluxed for 4 hours and stripped of solvent and volatiles in the usual manner.

Amongst the monoamines which may be used in the practice of the process of the present invention are hexadecyl amine, heptadecyl amine, octadecyl amine, nonadecyl amine, eicosyl amine, heneicosyl amine, heneicosenyl amine, docosenyl amine and the like.

In the preparation of the condensation products of the present invention, one may use any of the difunctional halohydrins, such as the epihalohydrins or the alpha-dihalohydrins. Specifically, one may use epichlorohydrin, epibromohydrin, epiodohydrin, or epifluorohydrin. Still further, one may make use of  $\alpha,\alpha'$ -dichlorohydrin,  $\alpha,\alpha'$ -dibromohydrin,  $\alpha,\alpha'$ -diiodohydrin, or  $\alpha,\alpha'$ -difluorohydrin. The following examples are set forth for the purpose of illustrating the process of applying the sizing material to the glass filaments, in keeping with the concept of the present invention. Any specific enumeration of detail is for the purpose of illustration only and should not be interpreted as a limitation on the case except as indicated in the appended claims.

#### Example 1

A plurality of glass filaments are drawn down from a conventional glass furnace at a rate of about 6,000–10,000 feet per minute and are passed rapidly over a sizing applicator roll which applies an aqueous dispersion of the sizing material produced according to condensation product A, referred to hereinabove, to the glass filaments. The filaments are then heated to cause the aqueous vapor portion of the sizing dispersion to become evaporated and the filaments become coated with the condensation product which has the desired sizing properties.

#### Example 2

Example 1 is repeated except that an aqueous dispersion of the sizing material prepared according to the example condensation product B is sprayed onto the hot filaments and the filaments are then heated, thus becoming coated with the sizing material as the water is flashed off.

If it is desired to combine with the fundamental sizes of the present invention, a resinous material, one may use to advantage thermosetting cationic melamine acid colloid resins, such as those described in U. S. Patent 2,345,543 to Wohnsiedler et al.; or, still further, one may modify the fundamental sizing material by mixing the same with thermosetting cationic amine-modified urea-formaldehyde resins, such as those described in U. S. Patents 2,471,188, 2,497,073–4, 2,546,575 and 2,554,475, amongst others.

If it is desired to produce a sizing material on the glass filaments in substitution for part or all of the fundamental sizing materials described hereinabove, one may make use of the resinous reaction product of a difunctional halohydrin in coreaction with an alkylene polyamine. To prepare such resinous materials, one would use the same difunctional halohydrins mentioned hereinabove in coreaction with alkylene polyamines such as 1,2-diamino ethane, 1,3-diamino propane, 1,4-diamino-n-butane, 1,5-diamino-n-pentane, 1,6-diamino-n-hexane, 1,10-diamino-n-decane, 1,6-diamino-3-methyl-n-hexane and the like. Amongst the polyalkylene polyamines which may be used in the preparation of the resinous sizing materials with the halohydrins are diethylene triamine, triethylene tetramine, tetraethylene pentamine,

propylene polyamines, such as di-3-amino-propylamine, pentaethylenhexamine, and the like. These resinous sizing materials will have application for certain specified purposes, wherein it is desired to have a hard coating on the glass filaments. These resinous sizing materials, however, tend to produce brittle films when used alone and, as a consequence, are not too desirable for all applications. Mixtures, however, of the condensation products of the higher monoamines with the halohydrins and the polyalkylene polyamine halohydrin resinous reaction products can be used to considerable advantage.

As a still further modification, one may use as a modifier for the fundamental sizing materials of the present invention, the condensation product produced by condensing a fatty acid containing from 14–22 carbon atoms with any of the alkylene polyamines referred to hereinabove. As the fatty acid component of such amides, one may use commercial mixtures of higher saturated fatty acids, for example, hydrogenated fatty acids of cottonseed oil, coconut oil fatty acids, or the acids from animal fats, such as tallow, lard and the like. A high proportion of saturated fatty acids is desired, such as mixtures containing at least 95% saturated acids. Thus, for example, the acids of hydrogenated tallow may be employed. Where a substantial proportion of fatty acids containing more than 18 carbon atoms is desired, hydrogenated fish oil fatty acids may be used. Hydrogenated talloil fatty acids may also be employed. For most purposes, we prefer to use those fatty acids having 16–18 carbon atoms, such as those derived from hydrogenated tallow since these are relatively low in cost and produce excellent sizing agents. Amongst the specific acids which may be used are myristic, palmitic, stearic, arachidic, behenic, and the like.

A still further modification of the fundamental sizes of the present invention can be accomplished by adding to the cationic halohydrin-amine condensation product varying amounts of polyvinyl alcohol, in which event the latter serves to insolubilize the halohydrinamine reaction product and further adds in contributing the film-forming characteristic of the polyvinyl alcohol to the fundamental sizes of the present invention. The insolubilization is probably due to the formation of a thermosetting material in which the cross linking takes place through the hydroxy groups of the polyvinyl alcohol.

In the preparation of the cationic sizing materials of the present invention, wherein one coreacts the halohydrins with the higher monoamines, the resultant condensation product may have a tendency to polymerize on storage thus reducing its storage stability. Since these condensation products have a pH of about 3–4 and tend to polymerize at pH's of 4 and higher, it is often desired to add a water soluble acidic material for the purpose of inhibiting the polymerization of the cationic halohydrin-amine condensation product in order to improve storage stability. To accomplish this, one should add about 0.5 mol of the water soluble acid material for each mol of the higher amine present in the condensation product so as to adjust the pH to about 2–3. Obviously, lesser amounts and greater amounts can be added depending upon the degrees of stability desired. Any water soluble acidic material may be added for the purpose of accomplishing this improved stability but it is preferred that organic acids be added such as acetic acid, propionic acid, and the like. Still further, one may make use of the water soluble inorganic acids such as hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid and the like or the water soluble acid salts derived therefrom such as sodium acid sulfate and the like. If these condensation products have been inhibited from further appreciable polymerization by the addition of an acidic material, it may be desired to render these condensation products at least slightly less acidic prior to, during or subsequent to their application to the glass filaments. To accomplish this, one may add a sufficient amount of alkaline material so as to adjust the pH of the sizing material solution to about 4.0 or higher although caution must be exercised if the solution is rendered less acidic before application on the glass filaments, not to raise the pH too high or precipitation from solution may result.

The fundamental sizes used in the practice of the process of the present invention are resinous in character and may be either thermoplastic or thermosetting depending on the mode of preparation. In the examples set forth hereinabove illustrating the process for the prep-

aration of these sizing materials, the thermoplastic resins were formed. This is accomplished by reacting the difunctional halohydrin with the monoamines simply by heating. A hydrohalide acid is given off which renders the reaction solution acidic. While the free acid is permitted to remain, only linear polymers may be formed which are thermoplastic in character. If one wishes to produce a cross linked polymer of thermosetting character, one would need only to neutralize some of the acid formed in the course of reaction by the addition of an alkaline material which would produce a salt and raise the pH of the solution, thereby permitting additional halohydrin to react with the amino group on the aliphatic monoamine. This results in a quaternization of the amino group which permits further reactivity with the halohydrin present thus forming a cross linked thermosetting material. To form the thermosetting material, it is necessary to use an excess of the halohydrin in addition to neutralizing the acid produced in the course of reaction. To produce the linear polymers, it is necessary to use at least equimolecular proportions and an excess will merely result in unreacted halohydrin.

We claim:

1. In a process for producing glass filaments, the steps comprising applying to said filaments, while in a comparatively hot condition, a sizing material comprising the condensation product of from 1-3 mols of a difunctional halohydrin with 1 mol of an aliphatic primary amine containing 16-22 carbon atoms and heating said sizing coated glass filaments.

2. In a process for producing glass filaments, the steps comprising applying to said filaments, while in a comparatively hot condition, a sizing material comprising the condensation product of from 1-3 mols of epichlorohydrin with 1 mol of octadecyl amine and heating said sizing coated glass filaments.

3. In a process for producing glass filaments, the steps comprising spraying said filaments, while in a comparatively hot condition, with an aqueous dispersion of a sizing material comprising the condensation product of from 1-3 mols of a difunctional halohydrin with 1 mol of an aliphatic primary amine containing 16-22 carbon atoms and heating said sizing coated glass filaments.

4. In a process for producing glass filaments, the steps comprising spraying said filaments, while in a comparatively hot condition, with an aqueous dispersion of a sizing material comprising the condensation product of from 1-3 mols of epichlorohydrin with 1 mol of octadecylamine and heating said sizing coated glass filaments.

5. In a process for producing glass filaments, the steps comprising passing said filaments, while in a comparatively hot condition, through an aqueous bath of a sizing material comprising the condensation product of from 1-3 mols of a difunctional halohydrin with 1 mol of an aliphatic primary amine containing 16-22 carbon atoms and heating said sizing coated glass filaments.

6. In a process for producing glass filaments, the steps comprising passing said filaments, while in a comparatively hot condition, through an aqueous bath of a sizing material comprising the condensation product of from 1-3 mols of epichlorohydrin with 1 mol of octadecyl amine and heating said sizing coated glass filaments.

7. Glass filaments coated with a sizing material comprising the condensation product of from 1-3 mols of a difunctional halohydrin with 1 mol of an aliphatic primary amine containing from 16-22 carbon atoms.

8. Glass filaments coated with a sizing material comprising the condensation product of from 1-3 mols of epichlorohydrin with 1 mol of octadecyl amine.

9. In a process for producing glass filaments, the steps comprising applying to said filaments, while in a comparatively hot condition, a mixture of (1) a sizing material comprising the condensation product of from 1-3 mols of a difunctional halohydrin with 1 mol of an aliphatic amine containing 16-22 carbon atoms and (2) a melamine-formaldehyde acid colloid resin and heating said mixture coated filaments.

10. In a process for producing glass filaments, the steps comprising applying to said filaments, while in a comparatively hot condition, a mixture of (1) a sizing material comprising the condensation product of from 1-3 mols of a difunctional halohydrin with 1 mol of an aliphatic amine containing 16-22 carbon atoms and (2) a cationic amine-modified urea-formaldehyde resin and heating said mixture coated filaments.

11. In a process for producing glass filaments, the steps comprising applying to said filaments, while in a comparatively hot condition, a mixture of (1) a sizing material comprising the condensation product of from 1 to 3 mols of a difunctional halohydrin with 1 mol of an aliphatic amine containing 16-22 carbon atoms (2) a melamine-formaldehyde acid colloid resin and (3) polyvinyl alcohol, and heating said mixture coated filaments.

12. In a process for producing glass filaments, the steps comprising applying to said filaments, while in a comparatively hot condition, a mixture of (1) a sizing material comprising the condensation product of from 1-3 mols of a difunctional halohydrin with 1 mol of an aliphatic amine containing at least 16-22 carbon atoms and (2) polyvinyl alcohol and heating said mixture coated filaments.

13. In a process for producing glass filaments, the steps comprising applying to said filaments, while in a comparatively hot condition, a mixture of (1) a sizing material comprising the condensation product of from 1-3 mols of a difunctional halohydrin with 1 mol of an aliphatic amine containing 16-22 carbon atoms (2) a cationic amine modified ureaformaldehyde resin and (3) polyvinyl alcohol, and heating said mixture coated filaments.

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