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## NOVEL SOLUTIONS OF POLY-(ACRYLIC ANHYDRIDE) AND POLY-(METHACRYLIC ANHYDRIDE) POLYMERS

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This invention relates generally to new compositions of matter, and specifically to homogeneous, ternary solutions in which one of the components is either a polymer of poly-(acrylic anhydride) or poly-(methacrylic anhydride).

As is generally known, films cannot be cast from polymeric substances, nor can fibers be fabricated therefrom by wet or dry spinning methods without a satisfactory capability for solubilizing the polymer. To our knowledge, this capability has not been provided heretofore for polymers of either poly-(acrylic anhydride) or poly-(methacrylic anhydride). This has been due to the unusual resistance of these polymers to the solvating action of known solvent systems. One explanation for this resistance is the suspected presence of cross-linking in the polymer structure. That is, in the polymerization of non-conjugated dienes to polymer products via a cyclic or intramolecular-intermolecular chain propagation mechanism, it is believed that to some extent cross-linking reactions occur as well as chain propagation reactions. In the polymerization via this mechanism of highly reactive dienes, such as acrylic or methacrylic anhydrides which contain ethylenically unsaturated double bonds conjugated with carbonyl double bonds, it is presumed that cross-linking reactions occur in the polymers formed. This could account for their insolubility in the solvents commonly employed for polymers of this general type.

It is, therefore, a principal object of this invention to provide a solvent mixture suitable for use in preparing solutions of poly-(acrylic anhydride) and poly-(methacrylic anhydride) polymers.

It is a further object of this invention to provide novel polymer containing ternary solutions which may be satisfactorily employed in film casting and fiber fabricating processes.

Other objects will become apparent in the description following.

The compositions meeting the afore-noted objectives are homogeneous ternary solutions comprising (A) from about 1 to 35 weight percent of a polymer selected from the group consisting of poly-(acrylic anhydride) and poly-(methacrylic anhydride); (B) from about 1 to 98 weight percent of a compound selected from the group consisting of dimethyl formamide, dimethylacetamide, dialkyl sulfoxides, aliphatic sulfones, lower aliphatic nitriles, lower aliphatic dinitriles, lactones and N-alkyl pyrrolidinones; and (C) from about 1 to 98 percent by weight of a compound selected from the group consisting of biuret, urea, lower alkyl ureas, thioureas, formamide, thioamides and amines having an ionization constant of from  $10^{-3}$  to  $10^{-14}$ .

As noted, the solvent employed in these novel solutions is a two component system. It is comprised of a compound selected from the group designated hereinabove merely for convenience as (B) together with a compound from the group designated above as (C). It will be recognized that group (B) compounds are known solvents for acrylic-type polymers, but will not, as such readily take polymers of poly-(acrylic anhydride) or poly-(methacrylic anhydride) into solution. Surprisingly, it has been found that when a group (B) compound is combined with those of group (C), with which they are miscible, a solvent system is obtained which is capable of forming clear

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homogeneous solutions of poly-(acrylic anhydride) and poly-(methacrylic anhydride) polymers with facility and without apparent limitation on polymer molecular weight. The solutions obtained when employing this novel solvent system fully meet the needs required for use in film casting and fiber forming processes.

These novel solutions are prepared merely by intermixing the various components of which they are comprised, i.e., the polymer solute and the two components which comprise the solvent. The order of mixing is not critical, i.e., the polymer can be mixed with one solvent component after which the second component may be added; or alternatively, a miscible mixture of the solvent components may be first prepared and the polymer added thereto. It is generally desirable to employ elevated temperatures, say up to  $150^{\circ}$  C., when forming the polymer solutions, although solutions can be formed at ambient temperatures. The advantage of an elevated temperature is merely a reduction in the time needed to accomplish complete solution.

For purposes of providing a more descriptive term for the solvent components, they will hereinafter be referred to as the "solvent" component and the "adjuvant" component, respectively. This is, the compounds noted above as belonging to the group (B) designation will be referred to as the "solvent" component while those previously designated as group (C) compounds will be referred to as the "adjuvant" component.

As the "solvent" component there may be employed, dimethyl acetamide and dimethyl formamide; dialkyl sulfoxides, such as dimethyl sulfoxide, diethyl sulfoxide, methylethyl sulfoxide, methyl isopropyl sulfoxide, tetramethylene sulfoxide and pentamethylene sulfoxide; aliphatic sulfones, for example, tetramethylene sulfone (sulfolane), cyclobutene sulfone (sulfolene) and dimethyl sulfone; lower aliphatic nitriles, such as glutaronitrile, succinonitrile, adiponitrile, 2-methyl glutaronitrile, 2-ethyl glutaronitrile and 2,2-dimethyl glutaronitrile; lactones such as  $\gamma$ -butyrolactone,  $\Delta$ -valerolactone,  $\epsilon$ -caprolactone,  $\beta$ -methyl- $\gamma$ -butyrolactone and N-alkyl pyrrolidinones, such as N-methyl pyrrolidinone, N-ethyl pyrrolidinone and 1,5-dimethyl-2-pyrrolidinone.

As the "adjuvant" component, there may be employed compounds, such as urea; lower alkyl ureas like dimethyl urea and tetramethyl urea; acetyl-urea; thiourea; thioamides, such as thioacetamide and N-methyl thioacetamide; formamide; biuret and amines having an ionization constant in the range of from  $10^{-3}$  to  $10^{-14}$ . The amines may be aliphatic cycloaliphatic, aromatic, primary, secondary or tertiary. Illustrative examples are triethylamine, tri-N-butylamine, pyridine, 2,6-dimethylpyridine, 2-chloropyridine, 2,4,6-triethylpyridine, aniline, dimethylaniline, diethylaniline, ethylmethylaniline, N-methylaniline, N-ethylaniline, o-toluidine, N-methyl-m-toluidine, o-toluidine and p-toluidine.

Although a satisfactory solvent system can be obtained by employing any of the noted "solvent" components in combination with one of the "adjuvants" described as suitable, a particularly outstanding combination is dimethyl formamide with pyridine.

As previously noted, the components making up the novel solutions of this invention may vary over a wide range in concentration. The particular amounts employed in any given instance will, of course, depend on the intended purpose. For example, when employing these solutions for fiber forming purposes a preferred concentration range by weight based on a percentage of the total weight of the solution is from 40 percent to 80 percent for the "solvent" component, from 5 percent to 25 percent for the "adjuvant" component and from 15 percent to 35 percent for the polymer.

In order to elucidate the invention in greater particu-