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CELLULOSE MIXED ESTER COMPOSITION

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This invention relates to compositions of matter in which mixed organic acid esters of cellulose are homogeneously mixed with an aryl phosphate such as triphenyl phosphate, with or without other useful addition agents, so that the resulting product will have properties such as will make the composition highly advantageous for use in the plastic and analogous arts such, for instance, as the manufacture of wrapping sheets, photographic film, artificial silk, varnishes or lacquers, molded products and the like.

One object of this invention is to produce a composition of matter which may be made into permanently transparent, strong and flexible sheets or films of desired thinness which are substantially waterproof, are unaffected by ordinary photographic fluids and possess the desired properties of a support for sensitive photographic coatings.

Another object of our invention is to produce a composition which is capable of easy and convenient manipulation in the plastic and analogous arts, such as in the manufacture of thin sheets suitable for wrapping articles of commerce, films, artificial silk filaments, varnishes, lacquers and the like; and to produce a composition which will not injure or be injured by, the substances or surfaces with which it is associated during manufacture, storage for use. Other and further objects will hereinafter become apparent to those skilled in the art to which this invention pertains.

We have found that when the mixed organic acid esters are colloidized or physically combined with a triaryl phosphate, the value of the resulting product is considerably enhanced for the various purposes mentioned above, as disclosed in our co-pending U. S. application Serial No. 179,177 filed Mar. 28, 1927, now U. S. Patent No. 1,880,808, of which this application is a continuation-in-part. The instant application is also in part a continuation of our copending application Serial No. 520,151, filed March 4, 1931 (later abandoned) disclosing mixed organic acid esters of cellulose plasticized with a plasticizer such as triphenyl phosphate and containing claims thereto. In addition to plasticizing the mixed esters of cellulose, the triaryl phosphates also have been found to materially reduce the inflammability of the mixed esters so that any danger from rapid burning in, for instance, its use as film becomes eliminated.

Any of the mixed organic acid esters of cellulose may be employed in our composition of matter, especially those contemplated in our co-pending U. S. applications 179,176 and 179,177, filed March 28, 1927, now U. S. Patents 1,800,860 and 1,880,808, respectively. However, any of the mixed organic acid esters known, have been found to produce valuable materials when combined with a triaryl phosphate. Methods of making mixed organic acid esters are common and are shown for example in the foregoing applications and patents and in the U. S. patents to Clarke and Malm, No. 1,698,048, 1,704,282, 1,735,159, U. S. Patent No. 1,651,991 to Berthon and British Patent No. 219,926 to Societe de Stearinerie et Savonnerie.

However, prior to our discovery, it was not recognized that these mixed esters of cellulose could be plasticized or that these esters were more compatible with the aryl phosphates than cellulose acetate. We have found that the aryl phosphates, when added to mixed organic acid esters of cellulose, do plasticize these esters and produce materials therefrom of highly desirable characteristics such as flexibility, stability, non-inflammability, smoothness, transparency, etc. The addition of aryl phosphates to cellulose acetate is well known, but cellulose acetate offers the disadvantage in this connection of permitting only a limited amount of triphenyl phosphate, for instance, to be incorporated therewith. This disadvantage obviously limits the number of combinations, for instance, of triphenyl phosphate and cellulose acetate which are possible, and consequently, the properties of cellulose acetate can only be improved to a certain extent. We have found the triaryl phosphates to be compatible with the mixed organic esters of cellulose in a far greater range of proportions than they are with cellulose acetate. We have prepared compositions containing as much triphenyl phosphate as the amount of cellulose ester present and they were found to be homogeneously combined. We have yet to find a combination of these ingredients which will not form a homogeneous composition. Whereas cellulose acetate is tolerant of only about 30% of its weight of triphenyl phosphate and about 20% of tricresyl phosphate, the mixed esters as exemplified by cellulose acetate-propionate are tolerant of an unlimited amount of triphenyl phosphate and of 50% or even more of tricresyl phosphate. Thus, the degree of softening of the cellulose mixed organic acid ester desired may be readily obtained. Other triaryl phosphates than those mentioned, such as monocresyl diphenyl phosphate, trinaphthyl phosphate, etc., also come within the scope of our invention.

Any of the mixed organic acid esters of cellulose may be employed in our composition of matter, especially those contemplated in our copending U. S. applications 179,176 and 179,177, filed March 28, 1927, now U. S. Patents 1,800,860 and 1,880,808, respectively. Some of the esters which we have found to be particularly suited for our composition of matter are:

Cellulose acetate-stearate, cellulose acetate-propionate, cellulose acetate-butyrate, cellulose acetate-stearate-palmitate, cellulose propionate-stearate, cellulose butyrate-stearate, cellulose acetate-crotonate, cellulose acetate-oleate, cellulose acetate-laurate, cellulose acetate-laurate-myristate.

From the above list, it may be noted that the mixed fatty acid esters of cellulose are particularly suited to our composition of matter. The term "fatty acid" as used herein is understood to include both the saturated and unsaturated series or, as they are commonly known, the acetic and the oleic acid series of acids.

In order that those skilled in this art may better understand our invention, by way of illustration the following is an example of a composition of matter which is quite suitable for the manufacture of photographic film or other sheets: about 100 parts of a cellulose acetate-propionate containing from 5–20% propionyl radical is dissolved with stirring at atmospheric temperature in about 400 parts of acetone. To this solution is then added 30 parts (or any amount desired for that matter) of triphenyl phosphate. The amount of plasticizer which one may use depends on the particular condition desired in the final product. For example, if one desires a softer, more pliable and flexible product than that obtained by employing 30 parts of triphenyl phosphate, a greater amount of plasticizer may be used. There need be no fear of incompatibility of the two ingredients when a larger amount of plasticizer is incorporated into a mixed organic acid ester of cellulose to form the product of our invention.

The following illustration discloses the compounding of a product which may be employed for the manufacture of a thin sheeting, for example, for wrapping purposes; 100 parts of a cellulose acetate-stearate having an acetyl content of about 40% is dissolved in about 500 parts of ethylene chloride. 10–20 parts of tricresyl phosphate may then be added to this solution although, as stated above, the degree of flexibility desired will determine the amount of plasticizer which should be incorporated.

In substantially the same manner as triphenyl phosphate is employed, we may also compound tricresyl phosphate with the mixed organic esters of cellulose except that not much more than 50 parts of tricresyl phosphate should be added to 100 parts of the mixed ester if it is desired to form a clear, transparent product as otherwise some separation of the tricresyl phosphate may occur on evaporating the solvent.

If desired, suitable quantities of other materials such as other cellulose esters or cellulose ethers, gums (natural or synthetic), waxes, heavy metal soaps, higher fatty acids or their esters with mono or polybasic alcohols, resins or oils may be added to our composition while it is still in solution.

A composition of matter, such as above described, may be deposited upon any suitable film forming surface to form a film or sheet, as is well known to those skilled in the art. A film so produced has permanent brilliancy, transparency and low inflammability, burning even less readily than ordinary newspaper. Such film is tough and flexible as shown by the fact that it will withstand many folds upon a modified Schopper fold-tester (commonly used for such purposes) without breaking and that even after being subjected for a number of weeks to air maintained at 65° C., the film still maintains flexibility, demonstrating that the film will withstand ordinary usage satisfactorily for years.

Other solvents such as ethylene chloride, ethyl acetate, chloroform-alcohol, etc., which are compatible with the particular mixed ester and plasticizer used, may be employed instead of acetone if desired. Also, instead of forming a composition of a single mixed ester and a single aryl phosphate, compositions may be produced in which mixtures of mixed esters and/or mixtures of various aryl phosphates may be employed. As stated before, simple esters may be incorporated in our composition together with mixed esters. In some cases the mixture of a simple and mixed ester results in a greater flexibility and resistance to moisture than is exhibited by either by itself.

The preparation of compositions of matter, or articles therefrom, by dissolving the cellulose mixed organic acid esters or the cellulose higher esters in ethylene chloride is not our joint invention but is the sole invention of Carl J. Malm, one of the applicants herein, as set forth in his application Serial No. 551,545, filed July 17, 1931.

In addition to its utility in the production of films and sheets, our composition of matter may also be employed with advantage in other branches of the plastic art. For example, our new composition of matter may be employed in the manufacture of artificial silk by the dry spinning method. It may be desired to employ a composition of different viscosity or evaporation characteristics, but this is a mere matter of changing the solvent proportion or adding evaporation retardants, such as higher alcohols or other higher or intermediate boiling constituents as has been well known in the art for more than a decade.

Our new composition of matter may be substituted to advantage for other cellulose derivative materials, in a number of the known lacquer formulas where they are compatible. Other uses within the scope of our invention will also suggest themselves to those skilled in the art such as the production of molded articles by heating under pressure a comminuted mixture of a mixed organic acid ester of cellulose and an aryl phosphate such as triphenyl or tricresyl phosphate.

What we claim as our invention and desire to secure by Letters Patent of the United States is:

1. A composition of matter adapted to be formed into a film or sheet, comprising a mixed organic acid ester of cellulose and an amount of a triaryl phosphate sufficient to increase the flexibility of said film or sheet substantially beyond the inherent flexibility of an unplasticized film or sheet of the mixed organic acid ester of cellulose, without substantially impairing its transparency.

2. A composition of matter adapted to be formed into a film or sheet, comprising a mixed organic acid ester of cellulose and an amount of a triaryl phosphate, selected from the group consisting of triphenyl and tricresyl phosphates, sufficient to increase the flexibility of said film or sheet substantially beyond the inherent flexibility of an unplasticized film or sheet of the mixed

organic acid ester of cellulose, without substantially impairing its transparency.

3. A composition of matter adapted to be formed into a film or sheet, comprising a mixed organic acid ester of cellulose, selected from the group consisting of cellulose acetate-propionate and cellulose acetate-butyrate, and an amount of triphenyl phosphate sufficient to increase the flexibility of said film or sheet substantially beyond the inherent flexibility of an unplasticized film or sheet of the mixed organic acid ester of cellulose, without substantially impairing its transparency.

4. A composition of matter adapted to be formed into a film or sheet, comprising a mixed organic acid ester of cellulose, selected from the group consisting of cellulose acetate-propionate and cellulose acetate-butyrate, and an amount of tricresyl phosphate sufficient to increase the flexibility of said film or sheet substantially beyond the inherent flexibility of an unplasticized film or sheet of the mixed organic acid ester of cellulose, without substantially impairing its transparency.

5. A composition of matter comprising a mixed organic acid ester of cellulose and 10–100% of triaryl phosphate.

6. A composition of matter adapted to be formed into a film or sheet, comprising a fully esterified mixed organic acid ester of cellulose and an amount of a triaryl phosphate sufficient to increase the flexibility of said film or sheet substantially beyond the inherent flexibility of an unplasticized film or sheet of the mixed organic acid ester of cellulose, without substantially impairing its transparency.

7. A transparent, flexible sheet comprising a mixed organic acid ester of cellulose and an amount of a triaryl phosphate sufficient to increase the flexibility of said sheet substantially beyond the inherent flexibility of an unplasticized sheet of the mixed organic acid ester of cellulose, without substantially impairing its transparency.

8. A transparent, flexible sheet comprising cellulose-acetate-propionate and an amount of a triaryl phosphate sufficient to increase the flexibility of said sheet substantially beyond the inherent flexibility of an unplasticized sheet of cellulose acetate-propionate, without substantially impairing its transparency.

9. A transparent, flexible sheet comprising a fully esterified mixed organic acid ester of cellulose and an amount of a triaryl phosphate sufficient to increase the flexibility of said sheet substantially beyond the inherent flexibility of an unplasticized sheet of the mixed organic acid ester of cellulose, without substantially impairing its transparency.

10. A transparent, flexible sheet comprising fully esterified cellulose-acetate-propionate and an amount of a triaryl phosphate sufficient to increase the flexibility of said sheet substantially beyond the inherent flexibility of an unplasticized sheet of cellulose acetate-propionate, without substantially impairing its transparency.

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