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COMPOSITION OF MATTER COMPRISING CELLULOSE ESTERS

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The present invention relates to a new composition of matter comprising cellulose esters of lower aliphatic carboxylic acids.

It is known that film-forming materials such as cellulose esters, in order to be suitable for the preparation of lacquers, coating materials and the like, require the incorporation therewith of resins. The presence within such film-forming materials of resins effects an increase of the adhesive properties of the films prepared therefrom if applied to a support and of the brightness of the coatings. Resins, in order to be suitable for the purpose in question, must be compatible with the film-forming materials within wide limits and, moreover, must be stable towards light to a far reaching degree. As far as cellulose esters of lower aliphatic acids are concerned, there is a lack of resins which combine these properties without being accompanied by other disadvantages. Thus, products of the condensation of formaldehyde and aromatic sulfonamides, such as benzene or toluene-sulfonamide, which have been mostly employed for the purpose in question, are relatively sensitive towards water, thus impairing the properties of the cellulose ester coatings. It is owing to this lack of suitable compatible resins that cellulose acetate and other cellulose esters with lower aliphatic acids, though being distinguished by an excellent fastness to light, have not been employed to a great extent within the coating and lacquer industry.

It is the object of our present invention to develop new resins which are compatible with such cellulose esters within wide limits and combine this compatibility with a good fastness towards water and light and with all such other properties as are required for the purpose in question. Other objects of our invention will be apparent from the following description and claims. Our invention in its broadest aspect relates to a composition of matter comprising cellulose esters of lower aliphatic carboxylic acids and formaldehyde-monoarylurea-condensation products. Condensation products of the character described are insoluble in aliphatic and aromatic hydrocarbons and soluble in those solvents such as ketones, esters, glycolmonoalkyl-ethers or chlorine containing hydrocarbons and alcohols which are usually employed for dissolving of cellulose esters. The softening point of such products is preferably between about 50 and about 100° C. They are capable of being homogeneously incorporated within cellulose esters up to a proportion of about 150%. Moreover, they are not materially colored and combine this property with a good fastness to light and to water. This is true of the pure monoarylurea-formaldehyde-condensation products as well as of those mixed condensation products which have been prepared from formaldehyde on the one hand and a mixture of a monoarylurea and another formaldehyde-reactive compound, provided that the monoarylurea is present therein in a preponderant amount. Suitable formaldehyde-reactive compounds for the purpose in question are, for instance, aryl-sulfonamides such as benzene- or toluyl-sulfonamide. As monoarylurea, there is preferred the non-substituted phenylurea, although substitution products thereof, such as a uniform toluyl-urea or xylyl-urea or mixtures of the isomeres thereof, are not excluded. Furthermore, there can be employed halogen-substituted phenyl ureas.

As cellulose ester, there is preferably employed the so-called secondary cellulose acetate, i. e. the product obtained from the primary cellulose triacetate by a partial saponification, furthermore, the primary cellulose triacetate itself, cellulose propionate and cellulose butyrate and mixed esters of the said acids.

As a matter of fact, the composition of matter described may also contain softeners such as triarylphosphates, trichloroethylphosphate, dialkylphthalates and, furthermore, pigments, dyestuffs, filling materials and the like.

The condensation products which are made use of in the preparation of our new compositions of matter can be prepared in the usual manner by causing formaldehyde to react upon a monoarylurea, the reaction being preferably started in an alkaline medium, for instance at a pH-value between about 8 and about 9, and finished at a pH-value between about 4 and about 8. The reaction temperature is preferably kept between about 60° and about 100° C, the condensation products being isolated from the aqueous medium by evaporation. Depending on the choice of the starting materials and on the degree of condensation, the softening point is between about 40 and about 110° C, the compatibility of the condensation products with cellulose esters being decreased with a rising of the softening point.

Our invention is furthermore illustrated by the following examples without, however, being restricted thereto, the parts being by weight:

Example 1

135 parts of phenylurea are heated for one hour at 90–100° C with 350 parts of a 33% solution of formaldehyde which has been rendered alkaline by means of sodium hydroxide. The resin thus formed is isolated by evaporating the water in vacuo. The heating in vacuo is continued until the resin has assumed a temperature of 120° C. The colorless resin having a softening point of 83–84° C according to the method of Krämer-Sarnow-Nagel is dissolved in cyclohexanone so as to form a 20% solution.

parts of this solution if added to an acetylcellulose lacquer of the following composition:

	Parts
Acetylcellulose	12
Methylacetate	9
Ethylacetate	4
Methanol	5
Ethylalcohol	15
Toluene	15
1-methoxy-2-acetoxy-ethane	40

yield a clear solution from which there is obtained after evaporation of the solvents a homogeneous clear film of an excellent adhesive capacity.

Example 2

405 parts of phenylurea are heated for half an hour at 95° C with 1050 parts of a 30% formaldehyde solution containing 1.5 parts of anhydrous sodium carbonate. After the addition of 2.25 parts of tartaric acid the solution is cooled to 50° C and filtered. By evaporating in vacuo at a temperature of 90° C, 500 parts of a colorless blistery resin are obtained. The following lacquer is prepared therefrom:

	Parts
Resin	8
Celluloseacetobutyrate	8
Tributylphosphate	2
Benzylbutylphthalate	2
Diglycolic acid butylene glycolic ester	0.5
Ferric hydroxide	8
Acetone	32.5
Toluene	13
Alcohol	4
Monomethylether of ethylene glycol	5
Acetic acid ester of monomethylether of ethylene-glycol	17

When this lacquer is applied onto a support either with a pencil or, after dilution with other solvents, by means of a spraying pistol, a well sticking, enamel-like lacquer is obtained.

Example 3

A resin having been prepared according to example 2 is melted in vacuo until a test portion of the same is brittle and no longer sticky at 20° C. Then, the resin is dissolved in an excess of hot propanol, freed from small impurities and concentrated so as to form a 70% solution. 7.5 parts of this resin solution are added to a solution of 7.5 parts of acetylcellulose in a mixture of

	Parts
Methylacetate	15
Methylalcohol	5
Ethylalcohol	11.3
Toluene	15
1-methoxy-2-acetoxy-ethane	35
Diglycolic acid butylene glycolic ester	1.7
Phthalic acid ester of monomethylether of ethylene-glycol	2

are still added thereto. The clear lacquer thus obtained is applied onto a plate of beechwood, the lacquer for the first coating being preferably somewhat more diluted with the same solvents in order to effect a better penetration of the wood. The lacquer thus obtained is distinguished by a good fastness to weather.

Example 4

100 parts of a 33% formaldehyde-solution are mixed with 7 parts of a 5% ammonia solution so as to assume a pH-value of 7.0. Then 32 parts of phenylurea and 8 parts of the urea from o-toluidine are dissolved therein at 70–80° C. The water is quickly evaporated by rising the temperature. There remains a light hard resin. This resin is capable of being homogeneously combined with acetylcellulose in the proportion of 3:4. The solution yields clear and hard, practically colorless films having a fastness to water which is better than that of pure acetylcellulose.

Example 5

To 120 parts of formaldehyde there are added 12 parts of a 4% ammonia solution and a mixture of 36 parts of phenylurea with 4 parts of benzenesulfonamide. The mixture is heated until a clear solution is reached, the pH-value being decreased to 5.5–6.0. Then the solution is evaporated in vacuo. The resin being formed at first and having a low melting point is heated until a test portion of the same is brittle at 90–100° C.

A solution of 100 parts of acetylcellulose is capable of taking up 140–150 parts of the resin. Clear, hard and quickly drying films are obtained from this solution.

Example 6

350 parts of a 33% formaldehyde-solution are neutralized with 36 parts of a 5% ammonia solution. 119 parts of phenylurea and 34 parts of o-toluenesulfonamide are dissolved therein at 70–80° C. The water is evaporated in vacuo. The resin is further heated at 90–100° C until it becomes hard. This resin obtained in a yield of 185 parts is almost colorless and compatible with acetylcellulose up to a proportion of 125:100. Hard, very bright and quickly drying lacquers can be obtained therewith.

Example 7

In the same manner as described in the foregoing example, there are condensed with formaldehyde 119 parts of phenylurea in admixture with 15 parts of benzenesulfonamide and 17 parts of p-toluenesulfonamide, 180 g of a colorless resin of the softening point 40° C being obtained thereby. It is compatible up to 200% with acetone-soluble acetylcellulose and yields therewith clear, hard and colorless lacquers. This resin is also compatible for 200% with celluloseacetobutyrate and yields therewith clear, very bright and colorless lacquers of a good fastness to light.

Example 8

1225 parts of a 33% formaldehyde-solution are neutralized with diluted ammonia solution. 332 parts of phenylurea and 165 parts of benzenesulfonamide are dissolved therein by heating. The resin being isolated as described in the foregoing examples has a softening point of 37° C and is compatible for 175% with celluloseacetate as well as with celluloseacetobutyrate.

Example 9

In 350 parts of a formaldehyde-solution being neutralized with diluted ammonia, there are dissolved while heating 82 parts of phenylurea and 63 parts of benzensulfonamide. The water is evaporated for the most part. Then toluene is added and the mixture is heated while constantly replacing the evaporating toluene until no more water evaporates. The toluene is also distilled off. There remain 160 parts of a hard yellow resin that can be combined for 100% with acetone-soluble celluloseacetate.

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