

UNITED STATES PATENT OFFICE

2,099,455

CELLULOSIC ARTICLE OF MANUFACTURE
AND METHOD FOR PREPARING SAME

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No Drawing. Application September 28, 1934,
Serial No. 745,976

2 Claims. (Cl. 106—40)

This invention relates to cellulosic structures such as filaments, threads, fabrics, sheets, films, caps, tubing, or the like. More particularly, this invention relates to cellulosic structures of the type just mentioned having a subdued or low luster and/or that are more or less opaque.

In the ordinary methods of preparing cellulosic structures, such as filaments, threads, films, caps, tubing, etc., from viscose, cuprammonium, nitro-cellulose, cellulose acetate and other cellulosic solutions (without the addition of opaquing and/or low luster-inducing agents to the solutions), the products are transparent or translucent and/or very highly lustrous. For many purposes, transparency, brilliant sheen and luster are not desirable and thus restrict the uses of the materials. Recently, various methods have been proposed for producing cellulosic structures having a low or subdued luster and/or opacity.

I have found that I can produce cellulosic structures characterized by a low luster and/or opacity by incorporating therein an organic ester of the character described in detail hereinafter which imparts opacity and/or low luster by remaining in the cellulosic structure.

An object of the invention comprises the production of new opacified and/or low luster cellulosic structures. A further object of the invention relates to the production of novel cellulosic structures containing organic compounds which remain in the finished article and which impart opacity and/or low luster. Other objects of the invention will appear hereinafter.

The objects of the invention are accomplished in general by incorporating in the cellulosic solution from which the structure is to be produced an opaquing and/or a low luster-inducing agent of the type hereinafter more fully explained.

The opacifying and/or low luster-inducing agent contemplated by this invention is an insoluble, solid, difficultly hydrolyzable ester of an organic hydroxy compound and an organic or inorganic acid which contains four or more carbocyclic or heterocyclic nuclei highly deficient in hydrogen, and which is substantially incompatible with the cellulosic solution from which the structure is to be produced.

So far as the instant invention is concerned, each closed chain of carbon or hetero-atoms or combination of carbon and hetero-atoms will be considered a nucleus. Thus, benzene, naphthalene and carbazole have one, two, and three nuclei respectively.

These opaquing and/or low luster-inducing agents, which are preferably white in color,

possess a sufficiently low vapor pressure and are sufficiently inert to resist the change or removal from the cellulosic structure in the ordinary process of making and finishing the same during the manufacture thereof. They also effectively resist removal or change during any of the usual processes to which the finished cellulosic structure may be subjected, such as boiling-off, dyeing, bleaching, washing, ironing, etc. These substances are incompatible with the mass of the substance constituting the final product. They may be soluble but, in the preferred embodiment of this invention, they are insoluble in the solution from which the structure is prepared.

Highly effective delusterants function in particular by reason of their opacifying power which is a function of the difference in refractive index between the delusterant particle and the surrounding medium. Those in my preferred range differ from the index of the medium by at least 0.10 and the greater this difference, the more effective the compound as an opacifier and/or delusterant. Most organic compounds have several indexes and the statement just made refers to the highest index of the compound or to any one of the several indexes.

It is furthermore of importance that the ester has a high degree of chemical stability to saponifying conditions such as the presence of 6% caustic at ordinary temperatures.

The esters considered as being within the scope of this invention may be prepared from various types of acids and alcohols, among which may be named the following:

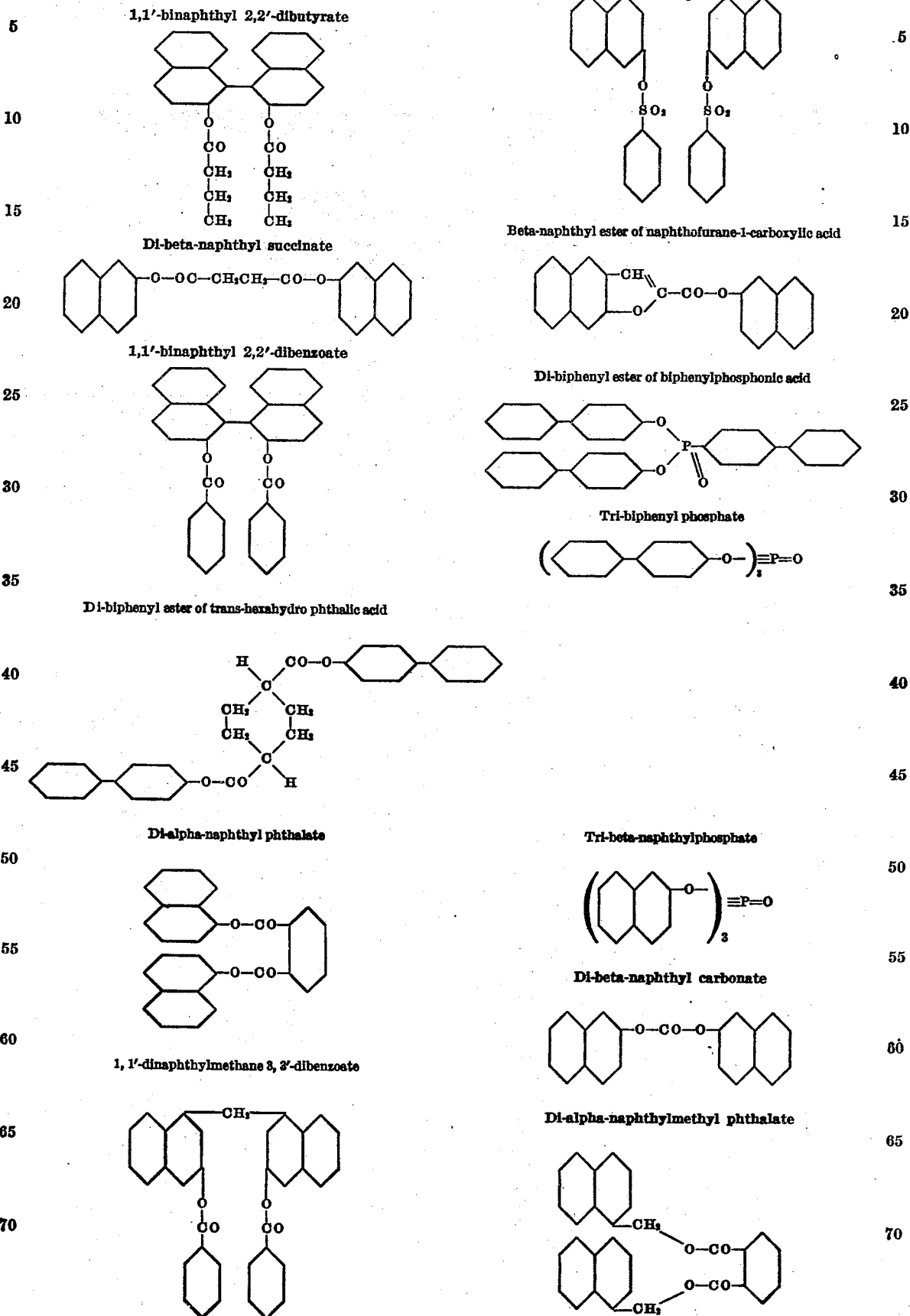
1. Types of acids:

- (a) Monobasic and polybasic carboxylic and thiocarboxylic acids, including aliphatic, alicyclic, aromatic and heterocyclic.
- (b) Sulfonic, sulfinic and phosphonic acids, including aliphatic, alicyclic, aromatic and heterocyclic.
- (c) Strictly inorganic acids such as carbonic and phosphoric.

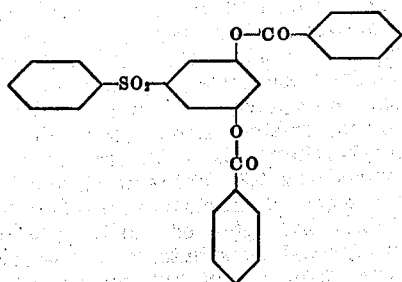
2. Types of alcohols, mono and polyhydric:

- (a) Aliphatic and alicyclic alcohols or substituted by aromatic or heterocyclic groups.
- (b) Aromatic and heterocyclic alcohols including those substituted by or joined by alkyl, aryl, aralkyl, halogen, alkyl, hydroxyl, -O-, -S-, -Se-, -Te-, -NH-, -SO₂-, -SO-, -CO-, -NR-, -NAr-, -NR-CO-R, -N(COR)₂, in which "R" may be an alkyl, aryl or alkaryl, or similar group.

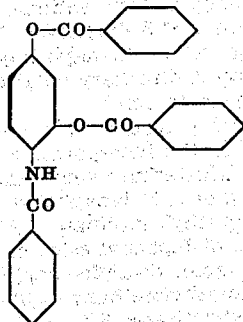
As illustrative examples of organic esters coming within the scope of the present invention the following may be mentioned:



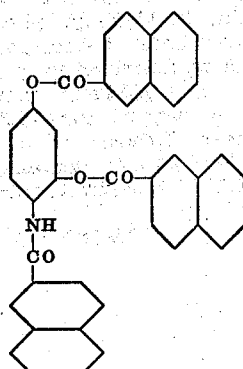
Di-benzoate of 3,5 hydroxyphenyl-phenyl sulfone



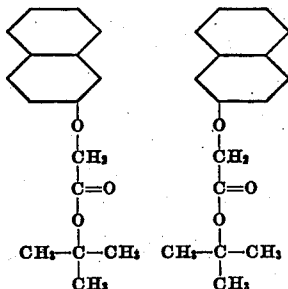
Di-benzoate of 4 benzoylamino-1,3-dihydroxy benzene



Di-beta-naphthoate of 4-beta-naphthyl amino-1,3-dihydroxy benzene



Ditertiary butyl ester of 1,1'-bi(2-naphthoxyacetic acid)



given satisfactory results, but, of course, it is obvious that smaller or larger quantities may be employed as desired. When a viscose solution is employed, satisfactory results may be secured if it contains 7% cellulose and from 0.01-1.5% more or less of the low luster-inducing and/or opa-

quing agent. If desired, the low luster-inducing agents contemplated by the instant invention may be used in combination with each other and/or with other low luster-inducing agents, such as mineral oil, petroleum jelly, waxes, paraffin, benzene, toluene, pine oil or inorganic pigments, such as titanium oxide, lithopone, zinc sulfide, etc.

The low luster-inducing agent may be added to the solution at any stage in the course of the manufacture thereof, or after the preparation of the solution and prior to the spinning, extrusion or casting operation. It may be added directly, if the particle size is satisfactory, or after suitable adjustment of the particle size by any of the well known methods, such as emulsification, grinding in a colloid mill or pebble mill, or in the form of a suspension or emulsion prepared with or without the assistance of suitable dispersing agents or protective colloids, such as soaps, sulfonated oils, alkyl naphthalene sulfonates, sodium caseinate, etc. or combinations thereof.

In order to more fully explain the principles of this invention, the following illustrative examples are given:

Example I.—Four hundred parts of 1,1'-dinaphthylmethane-3,3'-di-benzene sulfonate are ground with 600 parts of water, 8 parts of sodium caseinate, and 3,000 parts of pebbles in a pebble mill until the particles have been reduced to less than 4 microns in diameter. The resulting dispersion is used in making up viscose containing 7% cellulose in such proportions that 0.6% di-beta-naphthyl methane-di-benzene sulfonate is present. The resulting viscose solution is ripened and spun into rayon or cast into films in the usual manner. The products have a desirable opacity and low luster, far superior to that obtained with mineral oil and similar to that obtained with inorganic pigments.

Example II.—A sample of 1,1'-dinaphthylmethane-3,3'-di-acetate is ground, incorporated in viscose, and spun in the manner described in Example I. The resulting product has a desirable opacity and low luster.

Example III.—A sample of di-beta-naphthyl succinate is ground, incorporated in viscose and spun in the same manner described in Example I. The resulting product has a desirable opacity and low luster.

It is to be understood that these examples do not in any way restrict the invention thereto but merely illustrate several specific and preferred embodiments which have given satisfactory results.

Though the preferred embodiments of this invention contemplate the incorporation of the low luster-inducing agent in the solution at some time prior to the extrusion or casting thereof, satisfactory results may be secured also by applying the low luster-inducing agent to a previously formed cellulosic structure. In other words, the low luster-inducing agent may be incorporated in the final cellulosic structure by an after-treatment.

Though the invention has been specifically described in connection with the viscose process, it is obvious that the principles thereof are equally

Organic compounds of the character described which have a relatively high index of refraction and which are preferred on the basis of cost, color stability, acid insolubility and effectiveness are the following: Di-naphthylmethane-dibenzene sulfonate, di-beta-naphthyl succinate, di-naphthylmethane-di-acetate, di-naphthylmethane-dibenzoate, di-beta-naphthyl butyrate, and di-beta-naphthyl carbonate.

The quantity of the low luster-inducing and/or opa- quing agent which may be used may vary within wide limits, depending principally upon the opa- quing and luster desired in the final product. Cellulosic structures containing these low luster-inducing and/or opa- quing agents in amounts ranging from 0.10-20.0% by weight have

applicable to the cuprammonium cellulose, cellulose nitrate, and cellulose acetate processes.

In the case of cellulosic solutions of wholly organic solvents, it is only necessary that a suitable choice of organic ester be made so that the solubility characteristics do not interfere. It has already been pointed out that the low luster-inducing substance must be incompatible with the mass of substance constituting the final product. In addition, in the case of cellulose acetate or nitrate spinning solutions, it is preferable that the low luster-inducing substance be insoluble in the solvent employed. However, resinous materials and certain crystallized substances soluble in the solvent, precipitate, on the evaporation of the solvent, in the cellulose acetate in the form of fine amorphous or crystalline particles sufficiently small and well distributed to avoid harmful effect on the physical properties of the resulting structure. The advantage in such cases lies in avoiding the necessity for emulsifying or grinding the compounds to obtain suitable subdivision. Suitable compounds may be readily selected from any specific system by one skilled in the art.

While the invention has been described generally with respect to the use of the various compounds mentioned herein in opaquing cellulosic structures prepared by casting and/or spinning methods, it is desired to emphasize the fact that these compounds are of special benefit in the spinning of artificial silk. Thus, undelustered artificial silk has a shade and luster which is undesired for a great many purposes. In accordance with the present invention, it is possible to produce artificial silk, particularly of the regenerated cellulose type prepared from viscose or cuprammonium cellulose, having a pleasing dull appearance, the dullness being of any degree desired, in which the opaquing and/or delustering agent is uniformly distributed and which does not interfere with the tenacity of the yarn to any large extent.

Since it is obvious that various changes and modifications may be made in the above descrip-

tion without departing from the nature or spirit thereof, this invention is not restricted thereto except as set forth in the claims.

I claim:

1. A cellulosic structure containing a finely divided delustering agent taken from the group consisting of 1,1'-binaphthyl 2,2'-dibutyrate, di-beta-naphthyl succinate, 1,1'-binaphthyl 2,2'-dibenzoate, di-biphenyl ester of trans-hexahydro phthalic acid, di-alpha-naphthyl phthalate, 1,1'-dinaphthylmethane 3,3'-dibenzoate, 1,1'-dinaphthylmethane 3,3'-dibenzenesulfonate, beta-naphthyl ester of naphthofurane-1-carboxylic acid, di-biphenyl ester of biphenylphosphonic acid, tri-biphenyl phosphate, tri-beta-naphthylphosphate, di-beta-naphthyl carbonate, di-alpha-naphthylmethyl phthalate, di-benzoate of 3,5 hydroxyphenyl-phenyl sulfone, di-benzoate of 4 benzoylamino-1,3-dihydroxy benzene, di-beta-naphthoate of 4-beta-naphthoyl amino-1,3-dihydroxy benzene, ditertiary butyl ester of 1,1'-bi(2-naphthoxyacetic acid).

2. An artificial thread having low luster imparted thereto by the incorporation therein of a finely divided delustering agent taken from the group consisting of 1, 1'-binaphthyl 2,2'-dibutyrate, di-beta-naphthyl succinate, 1,1'-binaphthyl 2,2'-dibenzoate, di-biphenyl ester of trans-hexahydro phthalic acid, di-alpha-naphthyl phthalate, 1,1'-dinaphthylmethane 3,3'-dibenzoate, 1,1'-dinaphthylmethane 3,3'-dibenzenesulfonate, beta-naphthyl ester of naphthofurane-1-carboxylic acid, di-biphenyl ester of biphenylphosphonic acid, tri-biphenyl phosphate, tri-beta-naphthylphosphate, di-beta-naphthyl carbonate, di-alpha-naphthylmethyl phthalate, di-benzoate of 3,5 hydroxyphenyl-phenyl sulfone, di-benzoate of 4 benzoylamino-1,3-dihydroxy benzene, di-beta-naphthoate of 4-beta-naphthoyl amino-1,3-dihydroxy benzene, ditertiary butyl ester of 1,1'-bi(2-naphthoxyacetic acid).

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