

UNITED STATES PATENT OFFICE

2,099,441

CELLULOSIC PRODUCT AND METHOD FOR
PREPARING SAME

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4 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 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, nitrocellulose, cellulose acetate and other cellulosic solutions (without the addition of opaquing or low luster-inducing agents to the solutions), the products are transparent or translucent 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 or opacity.

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

An object of the invention comprises the production of new opacified 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 or low luster. Other objects of the invention will appear hereinafter.

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

The opaquing or low luster-inducing agent contemplated by this invention is a ketone or ketone resin having two or more cyclic nuclei highly deficient in hydrogen and in which the carbonyl group does not occur in the nuclei or in which only one carbonyl group is present in a single nucleus, and their colorless —O—R, —S—R, —Se—R, —Te—R, —NH—R, —R, hydroxy alkyl and halogen derivatives, in which "R" may be an alkyl, aryl, aralkyl, alkaryl or heterocyclic group.

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.

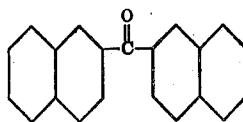
These opaquing or low luster-inducing agents, which are preferably white in color, possess a sufficiently low vapor pressure and are sufficiently inert to resist the change or removal from the cellulosic structure in the ordinary process of making and finishing the same during the manufacture thereof. 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 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.

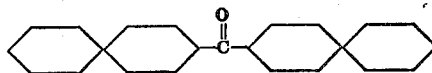
The following examples are illustrative of the ketones coming within the scope of this invention:

Non-cyclic ketones

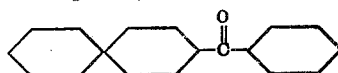
Di-naphthyl ketone



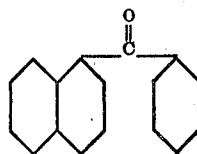
Di-biphenyl ketone

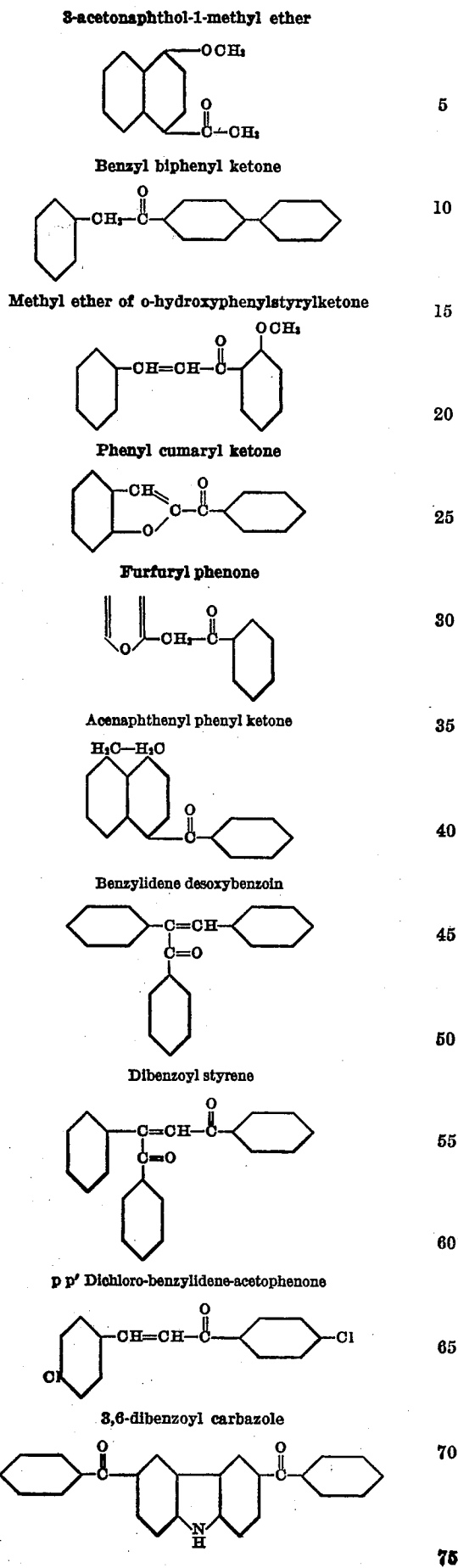
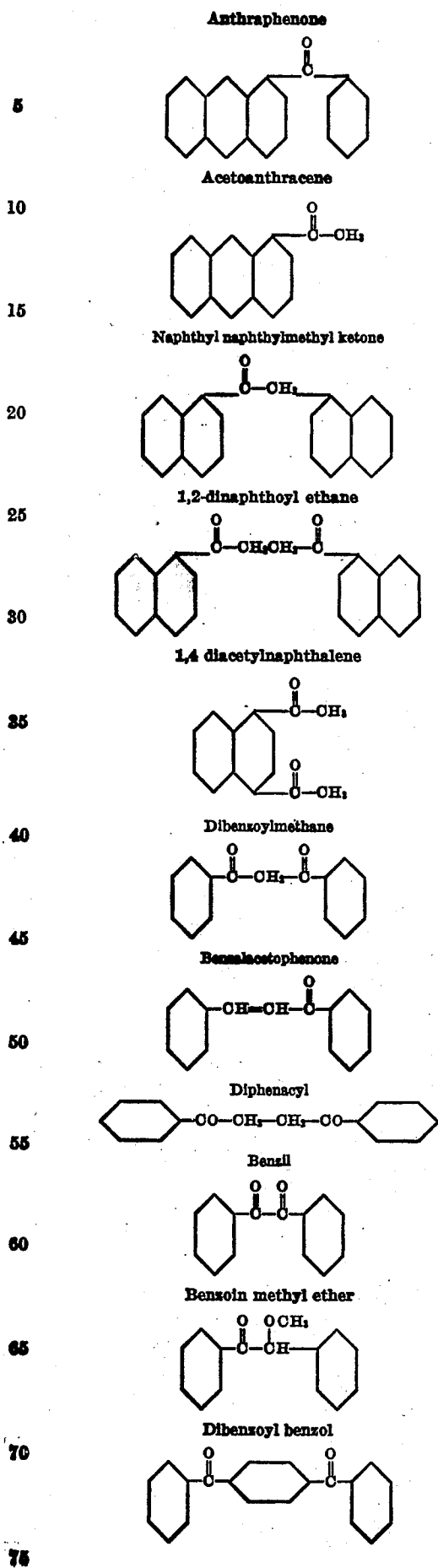


p-Phenylbenzophenone

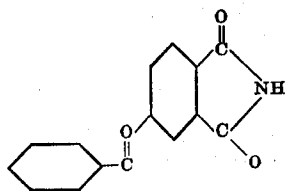


Naphthophenone

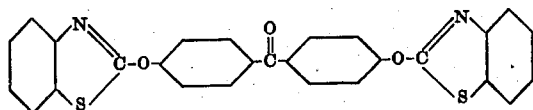




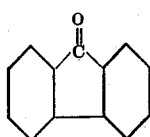
4, Benzoyl phthalimide



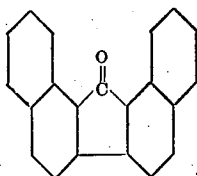
Dibenzthiazyl ether of diphenylol ketone

*Cyclic ketones*

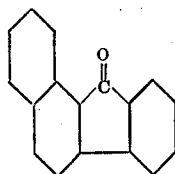
Diphenylene ketone



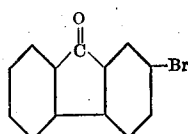
Dinaphthylene ketone



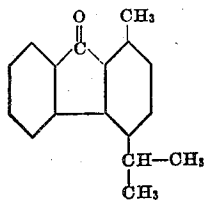
Chrysoketone



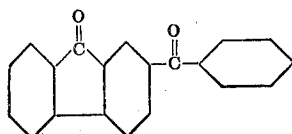
2-bromo-9-keto-fluoren



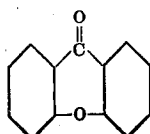
1-methyl 4-isopropyl diphenylene ketone



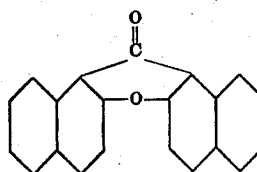
9-keto-2 benzoylfluoren



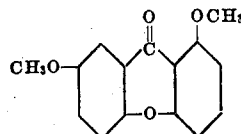
Xanthone



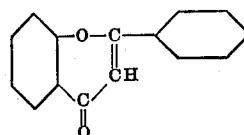
Dinaphthoxanthone



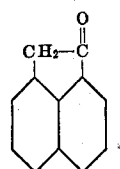
Euxanthone methyl ether



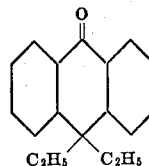
Flavon



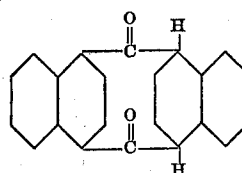
Acenaphthenone



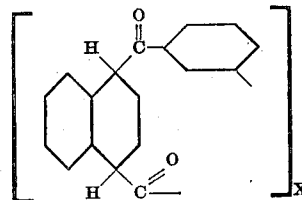
Diethyl anthrone



1,4 Naphthoyl-1,4 dihydronaphthalene



Ketone resin prepared by the condensation of 1,4 dihydronaphthalene 1,4-diacyl chloride with benzene



As further examples of ketones coming within the scope of this invention may be mentioned resins of ketones of the above mentioned types and the keto analogues of the ethers disclosed in my copending application Serial No. 673,315, filed May 27, 1933, and the copending application of Winfield W. Heckert and Miles A. Dahlen Serial No. 673,314, filed May 27, 1933.

The scope of this invention is not intended to include quinones in which two carbonyl groups are present in a single nuclei since such compounds are comparatively highly colored.

Ketones of the character described which have relatively high index of refraction and which are

preferred on the basis of cost, color stability, acid insolubility and effectiveness are the following:

Dinaphthyl ketone, naphthophenone, benzylidene-aceto-naphthone, furfural-aceto-naphthone, p-hydroxy benzophenone-formaldehyde resin, xanthone, di-biphenyl ketone.

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

If desired, the low luster-inducing agents contemplated by the instant invention may be used in combination with each other 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 diphenacyl (melting point 145°) are ground with 600 parts of water, 8 parts of sodium caseinate and 4000 parts of pebbles in a pebble mill until the particles have been reduced to a particle size below four microns in diameter. Sufficient of this slurry is used in making up viscose to include 0.6 to 1 per cent of diphenacyl in the viscose containing 7 per cent cellulose. The viscose is cast into films or spun in the usual manner. The products are characterized by a desirable opacity and low luster.

Example II.—A sample of di-beta-naphthyl ketone (melting point 164°) is ground and added to viscose in the manner described in Example I. The viscose is spun into rayon. A product is obtained which has a desirable low luster, much lower than is obtained with mineral oil, resembling in fact the product obtained by the use of mineral white pigments.

Example III.—A sample of p-p'dichlorobenzylidine acetophenone (melting point 157°) is treated as in Example I. The products are characterized by opacity and low luster.

Example IV.—Fifteen parts of di-biphenyl ketone are ground in a pebble mill with 50 parts of cellulose acetate and 700 parts of acetone and alcohol mixed in the ratio of 80 to 20, until most of the particles are below 4 microns in diameter. This dispersion is then employed in making up a cellulose acetate spinning solution in such propor-

tions that 1 part of di-biphenyl ketone is present for each 10 parts of cellulose acetate. The solution is spun into filaments or cast into films in the usual manner and the products have an unusually low luster and are highly opaque.

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

I claim:

1. Delustered cellulosic articles prepared from cellulosic solutions containing, in a phase distinct from the cellulosic material therein, a finely divided, white, delustering agent comprising a substance having two or more cyclic nuclei highly

deficient in hydrogen, said substance taken from the group consisting of di-naphthyl ketone, di-biphenyl ketone, p-phenylbenzophenone, naphthophenone, anthraphenone, acetonanthracene, naphthyl naphthylmethyl ketone, 1,2-dinaphthoyl ethane, 1,4 diacetylnaphthalene, dibenzoylmethane, benzalacetophenone, diphenacyl, benzil, benzoin methyl ether, dibenzoyl benzol, 3-acetonaphthol-1-methyl ether, benzyl biphenyl ketone, methyl ether of o-hydroxyphenylstyrylketone, phenyl cumaryl ketone, furfuryl phenone, acenaphthenyl phenyl ketone, benzylidene, desoxybenzoin, dibenzoyl styrene; p p' dichloro-benzylidene-acetophenone, 3,6-dibenzoyl carbazole, 4,benzoyl phthalimide, dibenzthiazyl ether of diphenylol ketone, diphenylene ketone, dinaphthylene ketone, chrysoketone, 2-bromo-9-keto-fluoren, 1-methyl 4-isopropyl diphenylene ketone, 9-keto-2-benzoylfluoren, xanthone, dinaphthoxanthone, euxanthone methyl ether, flavon, acenaphthenone, diethyl anthrone, 1,4 naphthoyl-1,4 dihydronaphthalene, ketone resin prepared by the condensation of 1,4 dihydronaphthalene 1,4-diacyl chloride with benzene.

2. Delustered cellulosic articles prepared from cellulosic solutions containing, in a phase distinct from that of the cellulosic material therein, a finely divided, white, delustering agent comprising 0.1 to 20.0% of a substance having two or more cyclic nuclei highly deficient in hydrogen, said substance taken from the group consisting of di-naphthyl ketone, di-biphenyl ketone, p-phenylbenzophenone, naphthophenone, anthraphenone, acetonanthracene, naphthyl naphthylmethyl ketone, 1,2-dinaphthoyl ethane, 1,4 diacetylnaphthalene, dibenzoylmethane, benzalacetophenone, diphenacyl, benzil, benzoin methyl ether, dibenzoyl benzol, 3-acetonaphthol-1-methyl ether, benzyl biphenyl ketone, methyl ether of o-hydroxyphenylstyrylketone, phenyl cumaryl ketone, furfuryl phenone, acenaphthenyl phenyl ketone, benzylidene, desoxybenzoin, dibenzoyl styrene, p p' dichloro-benzylidene-acetophenone, 3,6-dibenzoyl carbazole, 4,benzoyl phthalimide, dibenzthiazyl ether of diphenylol ketone, diphenylene ketone, dinaphthylene ketone, chrysoketone, 2-bromo-9-keto-fluoren, 1-methyl 4-isopropyl diphenylene ketone, 9-keto-2 benzoylfluoren, xanthone, dinaphthoxanthone, euxanthone methyl ether, flavon, acenaphthenone diethyl anthrone, 1,4 naphthoyl-1,4 dihydronaphthalene, ketone resin prepared by the condensation of 1,4 dihydronaphthalene 1,4-diacyl chloride with benzene.

3. An artificial thread having low luster imparted thereto by the incorporation therein of an incompatible, finely divided substance having

two or more cyclic nuclei highly deficient in hydrogen, said substance taken from the group consisting of di-naphthyl ketone, di-biphenyl ketone, p-phenylbenzophenone, naphthophenone, anthraphenone, acetonanthracene, naphthyl naphthylmethyl ketone, 1,2-dinaphthoyl ethane, 1,4 diacetylnaphthalene, dibenzoylmethane, benzalacetophenone, diphenacyl, benzil, benzoin methyl ether, dibenzoyl benzol, 3-acetonaphthol-1-methyl ether, benzyl biphenyl ketone, methyl ether of o-hydroxyphenylstyrylketone, phenyl cumaryl ketone, furfuryl phenone, acenaphthenyl phenyl ketone, benzylidene, desoxybenzoin, dibenzoyl styrene, p p' dichloro-benzylidene-acetophenone, 3,6-dibenzoyl carbazole, 4,benzoyl phthalimide, dibenzthiazyl ether of diphenylol ketone, diphenylene ketone, dinaphthylene ketone, chrysoketone, 2-bromo-9-keto-fluoren, 1-methyl 4-isopropyl diphenylene ketone, 9-keto-2 benzoylfluoren, xanthone, dinaphthoxanthone, euxanthone methyl ether, flavon, acenaphthenone diethyl anthrone, 1,4 naphthoyl-1,4 dihydronaphthalene, ketone resin prepared by the condensation of 1,4 dihydronaphthalene 1,4-diacyl chloride with benzene.

4. An artificial thread having low luster imparted thereto by the incorporation therein of an incompatible, finely divided substance having two or more cyclic nuclei highly deficient in hydrogen, said substance taken from the group consisting of di-naphthyl ketone, di-biphenyl ketone, p-phenylbenzophenone, naphthophenone, anthraphenone, acetonanthracene, naphthyl naphthylmethyl ketone, 1,2-dinaphthoyl ethane, 1,4 diacetylnaphthalene, dibenzoylmethane, benzalacetophenone, diphenacyl, benzil, benzoin methyl ether, dibenzoyl benzol, 3-acetonaphthol-1-methyl ether, benzyl biphenyl ketone, methyl ether of o-hydroxyphenylstyrylketone, phenyl cumaryl ketone, furfuryl phenone, acenaphthenyl phenyl ketone, benzylidene, desoxybenzoin, dibenzoyl styrene, p p' dichloro-benzylidene-acetophenone, 3,6-dibenzoyl carbazole, 4,benzoyl phthalimide, dibenzthiazyl ether of diphenylol ketone, diphenylene ketone, dinaphthylene ketone, chrysoketone, 2-bromo-9-keto-fluoren, 1-methyl 4-isopropyl diphenylene ketone, 9-keto-2 benzoylfluoren, xanthone, dinaphthoxanthone, euxanthone methyl ether, flavon, acenaphthenone diethyl anthrone, 1,4 naphthoyl-1,4 dihydronaphthalene, ketone resin prepared by the condensation of 1,4 dihydronaphthalene 1,4-diacyl chloride with benzene, said substance having an index of refraction differing by at least 0.1 from the index of refraction of the cellulosic medium of said structure.

WINFIELD WALTER HECKERT.