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CELLULOSIC STRUCTURE AND PROCESS FOR PREPARING SAME

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6 Claims. (Cl. 18—54)

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 which 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 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 aromatic hydrocarbon, having at least four nuclei, 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 low luster-inducing agent of the type hereinafter more fully explained.

The low luster-inducing agent, contemplated by this invention, is a hydrocarbon of high molecular weight comprising 4 or more carbocyclic nuclei highly deficient in hydrogen.

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

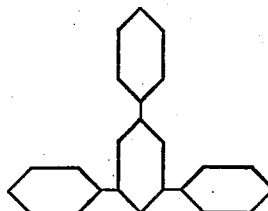
These opaquing and/or low luster-inducing agents, which are preferably white in color, possess a sufficiently low vapor pressure and are sufficiently inert to resist the change or removal from the cellulosic structure in the ordinary process of making and finishing the same during the manufacture thereof.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

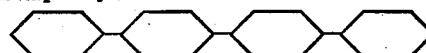
Highly effective delusterants function in particular by reason of their opacifying power which is a function of the difference in refractive index between the delusterant particle and the surrounding medium. Those in my preferred range differ from the index of the medium by at least 0.10 and the greater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

As illustrative examples of aromatic hydrocarbons comprising four or more nuclei, which come within the scope of this invention, are the following:

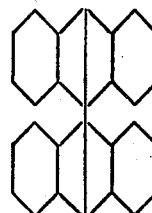
1,3,5-Triphenyl-benzene



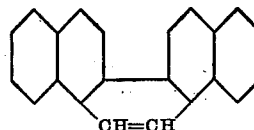
Bis(diphenyl)



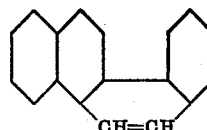
Bi-anthryl



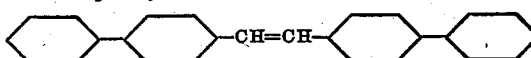
Picene



Chrysene

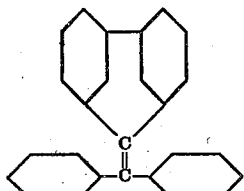


Bis(diphenyl) ethylene



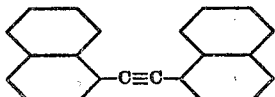
Diphenylene-diphenyl-ethylene

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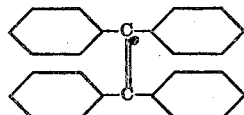
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Di-naphthyl acetylene



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Tetraphenyl-ethylene



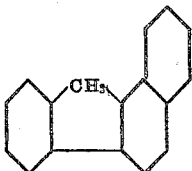
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Pyrene



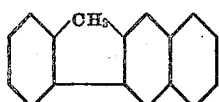
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Naphtho fluorene



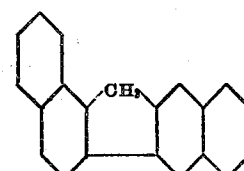
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Isonaphtho fluorene



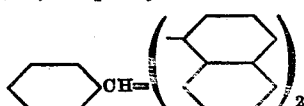
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Dinaphtho fluorene



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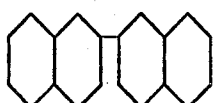
Phenyl(di 1,1 naphthyl) methane



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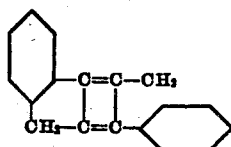
 α, α' dinaphthyl

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 β, β' dinaphthyl

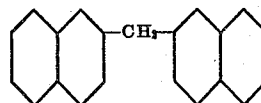
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Truxene



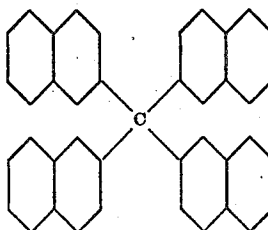
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Dinaphthyl-methane



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Tetranaphthyl methane

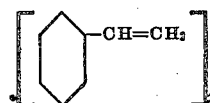


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The following resins which are hydrocarbon and aromatic in nature and which have at least 4 nuclei due to the condensation reaction which forms the resin, also fall within the scope of the invention:

Metastyrene



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Polybenzyl resins



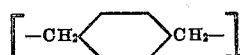
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Polyphenylene resins



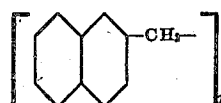
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Polyxylylene resins



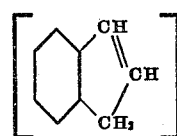
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Resins formed by condensing naphthalene and formaldehyde and one of which is available under the trade-name "Hyrax"



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Indene resins



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(In which x represents the number of chain units in the polymeric molecule).

Retene, which does not come within the strict definition of the invention as given above, may also be mentioned for use as a delusterant.

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It has been stated that opacifying power is a function of refractive index of the delusterant as compared with the medium. Rayon prepared by the viscose process has an average refractive index of 1.53 and by way of illustration in order to indicate the effectiveness of the high molecular weight hydrocarbons embraced within the scope of the present invention, 1,3,5-triphenyl-benzene, which has a maximum index of refraction of 1.873, has good opacifying power.

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The following examples illustrate modes of applying the principles of the invention:

Example I.—A naphthalene-formaldehyde resin is prepared by heating together at about 100° C. a mixture of naphthalene, formaldehyde, and

concentrated sulfuric acid in the ratios by weight of 25:3:4. The resin is purified by washing with water and taking up in an alcohol-benzene solution. Three pounds of the resin so prepared is dissolved in three pounds of benzene. This solution is emulsified with an equal volume of water using sulfonated castor oil as an emulsifying agent. For this purpose any high speed agitator or colloid mill is suitable which will reduce the emulsion average particle size to about 1 to 2 microns diameter. This emulsion is thoroughly incorporated with 1000 pounds of a viscose solution containing 7% cellulose. The viscose is ripened, filtered, etc., and spun in the usual way.

Example II.—Four pounds of metastyrene, prepared by polymerizing styrene at about 100° C., is ground as a water slurry to a particle size of about one micron diameter by means of a pebble or colloid mill. This slurry of dispersed resin is incorporated with 1000 pounds of a viscose solution containing 7% cellulose; the viscose is ripened, filtered, etc., and spun in the usual way.

Example III.—A naphthalene formaldehyde resin, such as may be prepared according to Example I is ground and dispersed in an 80-20 acetone-alcohol solution. A sufficient quantity of this solution is incorporated in the cellulose acetate solution to produce a thread, when spun therefrom by the dry spinning process, containing 5% naphthalene formaldehyde resin.

The quantity of the low luster-inducing and/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 and/or opaquing agents in amounts ranging from 0.10 to 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 and/or opaquing 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.

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 applied to the final cellulosic structure by an after-treatment and thus produce a delustered structure.

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 hydrocarbon or hydrocarbon resin 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 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 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. A cellulosic structure comprising a regenerated cellulose base containing incorporated therein 0.1 to 20% of a finely divided cyclic hydrocarbon having at least four cyclic nuclei, said hydrocarbon having a refractive index differing by at least 0.1 from the index of refraction of said cellulose base.

2. A cellulosic structure comprising a regenerated cellulose base containing incorporated therein 0.1 to 20% of a finely divided naphthalene-formaldehyde resin.

3. A cellulosic structure comprising a regenerated cellulose base containing incorporated therein 0.1 to 20% of a finely divided indene resin.

4. A cellulosic structure comprising a regenerated cellulose base containing incorporated there-

in 0.1 to 20% of a finely divided polymerized styrene.

- 5 5. A method of manufacturing delustered viscose rayon comprising dissolving in a fugitive hydrocarbon solvent a synthetic resin having an index of refraction substantially different from regenerated cellulose, admixing the resulting solution with viscose to effect dissemination of the resin throughout the viscose, and spinning the
- 10 viscose into regenerated cellulose filaments containing the resin in finely-divided form lending itself to the production of the desired delustering effect.

6. A cellulosic structure comprising a regener-

ated cellulose base containing incorporated 0.1 to 20% of a finely divided cyclic hydrocarbon taken from the group consisting of 1,3,5-triphenylbenzene, bis(diphenyl), bianthryl, picene, chrysene, bis(diphenyl)ethylene, diphenylene-diphenyl-ethylene, di-naphthyl acetylene, tetraphenyl-ethylene, pyrene, naphtho fluorene, isonaphtho fluorene, dinaphtho fluorene, phenyl(di 1,1 naphthyl) methane, α,α' dinaphthyl, β,β' dinaphthyl, truxene, dinaphthyl-methane, tetranaphthyl methane, metastyrene, polybenzyl resins, polyphenylene resins, polyxylene resins, naphthalene-formaldehyde resins and indene resins.

EMIL KLINE.