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CELLULOSIC STRUCTURES

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This invention relates to cellulosic structures, such as filaments, threads, fabrics, sheets, films, caps, tubing or the like, of either the regenerated cellulose or cellulose derivative type. More particularly, this invention relates to cellulosic structures of the type just mentioned having a subdued or low luster.

In the ordinary methods for producing cellulosic structures, such as filaments, threads, films, caps, etc. from viscose, cuprammonium, nitrocellulose, cellulose acetate and other cellulosic solutions (without the addition of low luster-inducing agents to the solutions), the products are transparent or translucent and/or very highly lustrous when compared to ordinary cotton fibers or natural silk. For many purposes the brilliant sheen and luster are not desirable and thus a limitation of the uses of the material results. Recently, methods have been proposed for producing cellulosic structures having a low or subdued luster. Certain of the suggested methods in connection with the production of artificial thread contemplated incorporating substances, such as inorganic pigments, mineral oils, certain fats, waxes, etc. in the spinning solution, and spinning the resulting solution. Other methods proposed spinning solutions in which materials, such as benzene, mono-chlorobenzene, aniline and other organic liquid solvents were incorporated, and these substances were either automatically removed during the process of producing the thread or deliberately removed from the formed thread by solvent or chemical action, vacuum or otherwise.

When the low luster-inducing substance remains in the thread, the reduction in the normal luster of materials of the type previously mentioned depends upon the index of refraction of the foreign substance added to the spinning solution. More particularly, the luster of the product depends upon the difference between the refractive indices of the foreign substance and the mass of the final cellulosic material in which said foreign substance in incorporated. The mean refractive index of rayon produced by the viscose process is usually considered to be 1.535 (1.52 and 1.55) and the index of refraction for cellulose acetate rayon is 1.48. Prior to the instant invention, the difference between the indices of refraction of organic materials incorporated in spinning solutions for the purpose of producing low luster materials and the substance constituting the mass of the product did not exceed approximately 0.07. Thus, in order to secure the extremely low lusters that are appropriate and desired for many purposes, the amounts of these organic low luster-inducing agents which are necessary are so great that spinning is impaired and the physical characteristics of the resulting thread so affected as to make the process impractical.

I have found that I can produce cellulosic structures, such as filaments, threads, sheets, films, caps, tubing and the like, of either the regenerated cellulose or cellulose derivative type, having a subdued or low luster and/or being opaque by incorporating in the solution from which the structure is prepared an organic substance, having an index of refraction differing by at least 0.1 from the mean index of refraction of the material constituting the mass of the structure and specifically a highly halogenated ring hydrocarbon, such as a highly halogenated derivative of benzene, diphenyl, naphthalene or anthracene, and which substance is non-fugitive, that is, it remains uniformly distributed substantially permanently throughout the mass of the cellulosic structure.

It is therefore an object of this invention to provide cellulosic structures having a subdued or low luster induced by an organic substance which has an index of refraction differing by at least 0.1 from the mean index of refraction of the substance constituting the mass of the thread and which is uniformly distributed throughout the mass thereof.

Another object of this invention is to provide cellulosic structures having a subdued or low luster induced by a highly halogenated ring hydrocarbon uniformly and permanently distributed throughout the mass thereof.

A specific object of this invention is to provide cellulosic structures having a low or subdued luster induced by a hexahalogenated benzene, such as hexachlorobenzene or hexabromobenzene, uniformly distributed throughout the mass thereof.

Another specific object of this invention is to provide cellulosic structures having a low or subdued luster induced by a highly chlorinated diphenyl uniformly distributed throughout the mass thereof.

A further specific object of this invention is to provide cellulosic structures having a low or subdued luster induced by a highly chlorinated naphthalene or highly chlorinated anthracene derivative uniformly distributed throughout the mass thereof.

Additional objects will appear from the following description and appended claims.

In accordance with the principles of the instant invention, there are provided cellulosic structures having a subdued or low luster and/or being more or less opaque. These desiderata are secured, according to one phase of the invention, by incorporating in the solution from which the structure is produced a low luster-inducing agent which remains substantially permanently in the finished product and is substantially uniformly distributed throughout the mass thereof. In so far as the invention is concerned, the low luster-inducing agent may be an organic solid or liquid, provided it possesses a sufficiently low vapor pressure and is sufficiently inert to resist change or removal from the structure in the ordinary process of making and finishing the structure during its manufacture. It must also effectively resist removal or change during any of the usual processes to which the finished structure may be subjected, such as boiling off, dyeing, bleaching, ironing, etc. It may be soluble but preferably insoluble in the solution from which the structure is prepared and should be incompatible with the mass of the substance constituting the final product.

The index of refraction of the low luster-inducing agent is, according to our invention, a highly important feature, and in accordance with this phase of the invention the low luster-inducing agent must have a refractive index of at least 0.1 above or below the mean refractive index of the cellulosic substance constituting the structure in which it is incorporated. By virtue of this characteristic, the low luster-inducing agent has a pronounced effect upon the final luster of the structure, reducing it to such an extent that the desirable low luster effects can be obtained using such small amounts of the low luster-inducing agent that spinning and physical properties of the product are not seriously impaired.

The final luster of the product is a function of the difference of the refractive indices of the low luster-inducing agent and the substance constituting the mass of the product. By virtue of this, if the difference is at least 0.1, the final luster, when compared to structures containing oils or the like, will be lower when the same quanties of low luster-inducing agents are employed in each case. Similarly, a luster equivalent to that secured with a certain amount of oil or the like will be obtained with a lesser quantity of the low luster-inducing substance of the instant invention.

The index of refraction of the low luster-inducing agent, in accordance with the instant invention, may be above or below that of the substance constituting the mass of the product, but, since most of the materials, because of the other chemical and physical properties (i. e. inertness, non-volatility, etc.) required have high refractive indices and since it is possible to obtain greater differences on the high side than on the low side of the substance constituting the mass of the product, I prefer to use low luster-inducing substances that have refractive indices greater than the substance constituting the product. To illustrate the foregoing in connection with the production of filaments, threads or films from viscose which have a mean refractive index of 1.535, the low luster-inducing agent should have a refractive index equal to or below 1.435 or 1.635 or above. The higher the refractive index above 1.635 and the lower below 1.435, the better the low luster. For filaments, threads or films formed of cellulose acetate, which as above explained has a refractive index of 1.48, the low luster-inducing agent should have a refractive index equal to or below 1.38 or 1.58 or above.

Referring to the subject of refractive index, it should be recognized that certain substances are isotropic and have only one refractive index. Other substances are anisotropic and have two or more refractive indices. In the case of an anisotropic substance, the significant value may or may not be the average or mean refractive index. In the case of an anistropic substance it is sufficient for any one of the refractive indices of the substance to differ from the refractive index of the mass of the material by at least 0.10 to fall within the scope of our invention. It is not necessary that each index of refraction or that the mean index of refraction differ by at least 0.10 above or below the mass of the material. Thus, an anisotropic substance of two refractive indices, say, 1.60 and 2.00, has a mean refractive index of 1.80. Such a substance would obviously fall within the scope of our invention when used, for instance, in the production of regenerated cellulose structures because the mean index is more than 0.1 higher than that of the mass material, even though one of the indices (1.60) is less than 0.1 above that of the mass. Since the other index in this case is 2.00, this substance, for the purpose of this invention, also has a refractive index more than 0.40 higher than that of the mass of the material. An anisotropic substance with indices 1.50 and 1.70, on the other hand, has a mean index of only 1.60 but it has one index (1.70) more than 0.10 higher than the mass and, hence, it also comes within the scope of the invention.

As examples of substances possessing the aforementioned characteristics and particularly suitable for the purpose may be mentioned the highly halogenated ring hydrocarbons having high melting and/or boiling points and including highly halogenated benzene, naphthalene, anthracene and diphenyl. It is to be noted that as the degree of halogenation is increased, the refractive indices of ring hydrocarbons ordinarily increase. Consequently, the low luster-inducing effects are increased.

In one of the preferred embodiments of this invention the highly halogenated hydrocarbon is a completely halogenated compound, i. e. each hydrogen being substituted by halogen. Such compounds are further characterized by (1) no hydrogen in the molecule, (2) greater chemical stability, (3) still higher refractive index and (4) reduced odor (at least in certain cases).

The hexahalogenated benzene derivatives, such as hexachlorobenzene and hexabromobenzene, are suitable and useful. The refractive indices of hexachlorobenzene are approximately 1.55 and 1.87, while the indices of refraction of hexabromobenzene are approximately 1.66 and 1.95. The highly chlorinated diphenyls which are currently sold under the trade name "Aroclors" are specific examples of halogenated diphenyls which are satisfactory as low luster-inducing agents. Among these, "Aroclor" #1268, having refractive indices of approximately 1.64 and 1.75 and "Aroclor" #4465 having a refractive index of approximately 1.66 are satisfactory. Good results are also secured by using highly chlorinated naphthalene derivatives currently sold under the trade name of "Halowaxes", particularly "Halowax" #1014 having refractive in-

dices of approximately 1.51 and 1.79 and "Halowax" HXRD 2–25 having refractive indices of approximately 1.48 and 1.81. The "Aroclors" and "Halowaxes" specifically named are more or less resinous solids varying in color from a light brown to pale yellow and are to be distinguished from the lower halogenated diphenyls and naphthalenes which are liquid, volatile and possess comparatively low refractive indices.

It is to be noted that the refractive indices of the substances set forth in the paragraph immediately preceding are approximate.

It is to be understood that the highly halogenated ring hydrocarbons may be used in combination with themselves or with mineral oils, etc. as well as in combination with inorganic pigments, such as titanium oxide, xinc sulfide, etc. in order to secure desirable opaquing and low luster effects. In all cases where combinations of low luster-inducing agents having refractive indices above and below that of the cellulosic substance constituting the mass of the structure are used, the low luster-inducing agents should preferably be immiscible. When a combination of low luster-inducing agents having refractive indices on the same side as the mass of the structure is used, the agents may or may not be miscible. When combinations of low luster-inducing agents are employed, the low luster effects may or may not be the same as that produced by a single substance having a refractive index equal to the mean refractive index of the two individual substances.

The particle size of the low luster-inducing agent is of extreme significance from the point of view of the low luster effects produced. It is to be understood that I am not concerned with the smallest possible particle size nor that particle size necessary for optimum spinning. In addition to the refractive index difference between the low luster-inducing agent and the mass of the substance constituting the structure, there is an optimum particle size for every substance (which can easily be determined by simple experiments) which aids in producing maximum and optimum low luster effects. This optimum size varies for different materials and represents a minimum size beyond which it is not desirable to go for optimum low luster effects. It is, however, sufficiently small to permit good spinning in the manufacture of artificial thread. For example, with hexachlorobenzene, best results are secured when the particle size thereof is approximately 1 micron in diameter. The optimum particle size of the chlorinated diphenyls and the chlorinated naphthalenes is approximately 1–2 microns in diameter.

The quantity of low luster-inducing agents used may vary within wide limits depending chiefly upon the differences in refractive index between that of the low luster-inducing agent and that of the substance constituting the mass of the structure, upon the opaquing and luster desired as well as upon the particle size. Cellulosic structures containing low luster-inducing agents in amounts ranging from 0.14% to 21% by weight may be produced satisfactorily but smaller or larger quantities may be employed if desired. A viscose solution containing 7% cellulose and from 0.01% to 1.5% of the low luster-inducing agent gives satisfactory results but smaller or larger quantities may be used if desired.

The low luster-inducing substances may be added to the cellulosic solutions at any stage in the course of the manufacture or after the preparation of the solution and prior to the time that it is spun or cast. It may be added directly if the particle size is satisfactory or after suitable adjustment of particle size by any of the well-known methods, such as 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, sulphonated oils, alkyl naphthalene sulphonic acid salts (Nekals), sodium caseinate, etc. As previously explained, it may be added alone or in combination with mineral oil or organic substances, such as benzene, etc. or inorganic pigments, such as titanium oxide, zinc sulphide, etc. or with other similar organic substances.

It is to be noted that the indices of refraction of the low luster-inducing substances differ from the cellulose structure by at least 0.1, such as for example 0.10, 0.15, 0.20, 0.30, 0.40, etc. It is to be understood that the greater the difference between the indices of refraction of the material, the greater will be the final low luster effect.

In order to more clearly describe the invention, the following specific examples are set forth. It is to be understood that these examples are not intended to be limitative of the invention but are merely for the purpose of illustrating several specific embodiments which have been found to produce satisfactory results.

Example 1.—1 pound of hexachlorobenzene is ground in a pebble mill with about 2 pounds of water containing a small amount of a suitable dispersing agent, such as sodium caseinate or sulphonated castor oil, until the mean particle size is reduced to approximately 1 micron in diameter. The suspension thus obtained is added to 97 pounds of viscose containing sufficient cellulose, caustic and water so that the composition of the final solution after the addition of the hexachlorobenzene will be 7% cellulose, 6% NaOH, and 1% hexachlorobenzene. The hexachlorobenzene is thoroughly incorporated and distributed throughout the viscose by suitable mixing, circulation and/or homogenization. The viscose is ripened, filtered and spun in the regular way. The resulting thread after regular processing has a permanent and desirable dull luster that is considerably lower than could be produced by an equivalent weight of mineral oil in viscose.

Example 2.—0.5 pound of hexabromobenzene is ground in a pebble mill with about 2 pounds of water as described in Example 1 to a particle size of approximately 0.75 micron in diameter and incorporated in viscose to produce a solution containing 7% cellulose, 6% NaOH, and 0.5% hexabromobenzene. The viscose is processed in the usual way as described in Example 1.

Example 3.—In chlorinating diphenyl, under certain conditions, a pale yellow, hard, crystalline mass is obtained which has a softening point of 127° C.–171° C., boiling point 395° C. to 415° C., density 1.8, refractive indices of 1.64 and 1.75. This chlorinated diphenyl is dispersed in one of many ways until the mean particle size is approximately 1.4 microns in diameter. This reduction in particle size may be accomplished by pebble mill grinding, by processing through a colloid mill, or by emulsifying a benzene or similar solution of the material in water using a suitable protective colloid. The suspension obtained is added and incorporated into viscose

using such amounts of the diphenyl in viscose as to produce a solution containing 1.5% of the chlorinated diphenyl, 7% cellulose, and 6% NaOH. The resulting viscose is processed and spun in the usual way.

Example 4.—In chlorinating naphthalene, under certain conditions, a pale yellow, crystalline mass is obtained with specific gravity of 1.74 at 150° C., melting point of about 130° C., boiling point of about 370° C. and refractive indices of 1.51 and 1.79. This chlorinated napthalene is reduced in particle size to approximately 1.5 microns in diameter and dispersed as described under Example 3 above and incorporated in viscose, using such amounts of the chlorinated naphthalene in viscose as to produce a solution containing 7% cellulose, 6% NaOH, and 1.0% chlorinated naphthalene. The viscose is processed and spun in the usual way.

Example 5.—The procedures described in Examples 1 and/or 2 above are carried out and the viscose cast into films, sheets, or formed into caps, bands, etc. in the usual way for the production of these types of structures.

Example 6.—Hexachlorobenzene of suitable particle size is incorporated into a solution of cellulose acetate in a suitable solvent in such an amount as to produce a solution containing 25% cellulose acetate and 3% hexachlorobenzene. The solution is then processed and spun in the usual way.

Since it is obvious that various changes may be made without departing from the nature of the invention, I do not limit myself to the exact specific details above set forth except as defined in the following claims.

I claim:

1. A cellulosic structure characterized by a subdued or low luster and having a finely divided completely halogenated ring hydrocarbon compound uniformly distributed throughout the mass thereof, said compound consisting of a ring hydrocarbon in which each hydrogen in the molecule has been substituted by halogen and being sufficiently inert to resist change or removal during the process of preparing the structure and the usual operations to which the structure may be subjected in use.

2. A cellulosic structure characterized by a subdued and low luster and having a finely divided hexahalogenated benzene uniformly distributed throughout the mass thereof.

3. A cellulosic structure characterized by a subdued and low luster and having finely divided hexachlorobenzene uniformly distributed throughout the mass thereof.

4. A cellulosic structure characterized by a subdued and low luster and having a finely divided completely chlorinated naphthalene uniformly distributed throughout the mass thereof.

5. A regenerated cellulose structure characterized by a subdued or low luster and having a finely divided completely halogenated ring hydrocarbon compound uniformly distributed throughout the mass thereof, said compound consisting of a ring hydrocarbon in which each hydrogen in the molecule has been substituted by halogen and being sufficiently inert to resist change or removal during the process of preparing the structure and the usual operations to which the structure may be subjected in use.

6. A regenerated cellulose structure characterized by a subdued and low luster and having a finely divided haxahalogenated benzene uniformly distributed throughout the mass thereof.

7. A regenerated cellulose structure characterized by a subdued and low luster and having finely divided hexachlorobenzene uniformly distributed throughout the mass thereof.

8. A regenerated cellulose structure characterizer by a subdued and low luster and having a finely divided completely chlorinated naphthalene uniformly distributed throughout the mass thereof.

9. As a new article of manufacture, delustered rayon containing distributed particles of hexachlorobenzene.

10. Cellulosic artificial silk filaments or threads characterized by a subdued or low luster and having a finely divided completely halogenated ring hydrocarbon compound uniformly distributed throughout the mass thereof, said halogenated hydrocarbon consisting of a ring hydrocarbon in which each hydrogen in the molecule has been substituted by halogen and being sufficiently inert to resist change or removal during the process of preparing the filaments or threads and the usual operations to which the structure may be subjected in use.

11. Cellulosic artificial silk filaments or threads characterized by a subdued or low luster and having a finely divided completely chlorinated benzene uniformly distributed throughout the mass thereof.

12. Cellulosic artificial silk filaments or threads characterized by a subdued or low luster and having a finely divided completely chlorinated naphthalene uniformly distributed throughout the mass thereof.

13. Regenerated cellulose artificial silk filaments or threads characterized by a subdued or low luster and having a finely divided completely halogenated ring hydrocarbon compound uniformly distributed throughout the mass thereof, said halogenated hyrocarbon consisting of a ring hydrocarbon in which each hydrogen in the molecule has been substituted by halogen and being sufficiently inert to resist change or removal during the process of preparing the filaments or threads and the usual operations to which the structure may be subjected in use.

14. Regenerated cellulose artificial silk filaments or threads characterized by a subdued or low luster and having a finely divided completely chlorinated benzene uniformly distributed throughout the mass thereof.

15. Regenerated cellulose artificial silk filaments or threads characterized by a subdued or low luster and having a finely divided completely chlorinated naphthalene uniformly distributed throughout the mass thereof.

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