This invention relates to a method of producing rayon and more particularly it relates to an improved method of producing rayon having a low luster.

Rayon having a subdued luster may be made by several methods. In one method, a pigment, usually titanium dioxide, is incorporated in the spinning solution. This method is fairly effective in producing yarns of reduced luster, but for yarns of very low luster, the quantity of pigment required is such that the yarn is weakened appreciably and the solution has an abrasive action on the spinning orifice. In addition, as is well known, yarns delustered by pigments regain their luster upon being dyed to a dark color since the pigment has little effect upon the smoothness of the filament surface.

In another method, an immiscible liquid is dispersed in the spinning solution, and the rayon is spun and finished in substantially the usual manner. This method of deluster ing depends for its effect on the roughness produced in the surface of the filament and is thus effective on dark or light yarns. Refined mineral oil may be used as the delusterant. However, dispersions in viscose are unstable; the particles agglomerate and produce breaks or weak spots in the filament. For this reason, it is very difficult to produce low denier filaments from viscose containing mineral oil as the deluster ing agent. Pine oil, which forms more stable dispersions in viscose, may be used to overcome this disadvantage. However, pine oil delusters only partially to a poorly opalescent et, rather than to a completely dull state and furthermore it has a persistent residual odor which is difficult to remove. Mineral and pine oil both impart a slightly yellowish cast to rayon in which they are used as delustering agents.

It is an object of this invention to provide a method of producing rayon of reduced or low luster or rayon which is without luster in a simple and expedient manner, without, at the same time, unduly weakening the rayon or imparting an undesired odor.

It is a further object to provide a method of producing odorless rayon which is substantially without luster or of reduced luster whether the rayon is white or dyed a dark color or black and still further to produce such rayon in a type having low denier filaments.

It is still another object to provide a method of producing rayon of reduced luster characterized by a pleasing whiteness.

These objects are accomplished according to this invention, by spinning rayon from a viscose solution containing a dispersed delusterant composition comprising a terpene ether. The viscose is coagulated and the rayon finished in the usual manner.

The terpene ether utilized in the delusterant composition in the improved method of this invention is characterized by containing an ether linkage connecting a terpene group with a second group. It may be prepared by the etherification of the hydroxyl group of a terpene alcohol with another alcohol, or it may be prepared by the direct addition of an alcohol at a double bond of an unsaturated terpene group of a terpene compound. The alcohol used as an etherifying agent may be, for example, methyl, ethyl, propyl, butyl, amyl, beta-chloroethyl, chloro-propyl, isopropyl, isobutyl, secondary butyl, furyl, tetrahydrofurfuryl, benzyl alcohol, the monomethyl or monoethyl ether of ethylene glycol or of diethylene glycol, and so forth. The alcohol may be dihydric, for example, ethylene glycol, diethylene glycol, propylene glycol, etc., which allows two terpene groups to form ether linkages to the alcoholic group, if this is desired.

The terpene alcohol used to prepare the terpene ether may be any terpene alcohol having a reactive hydroxy group, such as, for example, alpha-terpineol, borneol, fenchyl alcohol, etc. Crude cuts rich in such terpene alcohols or mixtures thereof, pine oil for example, may likewise be etherified.

The unsaturated terpene compounds used to prepare the terpene ether by the addition of an alcohol at a double bond may be, for example pinene in alpha or beta form, dipentene, terpinene terpinolene, camphene, bornylene, myrcene, allo-calamene, sesquiterpenes, polyterpenes, etc. Crude mixtures, i.e. terpene cuts such as turpentine, for example, may be used and in general it is not essential that the resulting crude ether be highly purified for use in the method according to this invention. For example, the ether formed by the addition of methyl alcohol to pinene may be made by reacting methyl alcohol with turpentine. The ether of a terpene or terpene compound and an alcohol is termed herein and in the claims, for convenience, "a terpene ether."

In producing rayon characterized by reduced luster in accordance with this invention, one or more terpene ethers is introduced into the viscose prior to the spinning thereof. The terpene ether may be dispersed directly in the viscose or it may be added to the sodium hydroxide, water, and cellulose xanthate mixture used to make the viscose. If desired, the substance may first be emulsified in water and the emulsion then mixed with the viscose or its ingredients. If desired, emulsifying agents such as, for example, sodium oleate, sulphonated vegetable oils, Turkey red oil, Monopole oil, synthetic wetting agents, etc., may be used to aid in preparing such an emulsion. Preferably, the dispersed particles of the
The quantity of delusterant substance added depends upon the degree of luster desired in the rayon. Luster decreases as the quantity of delusterant substance is increased. The quantity of terpene ether or ethers utilized as delusterant may be varied from about 0.05% by weight to about 5% by weight of the viscose solution.

After the delusterant substance is dispersed in the viscose, the viscose is spun and the thread produced therefrom is finished in the usual manner. The dispersion of a terpene ether in viscose is quite stable so that the viscose may stand for a considerable time, say up to 60 or more hours, without spinning difficulties being encountered due to agglomerations of the dispersed particles.

The finishing operations, i.e., washing, desulphurizing, bleaching, drying, etc., remove substantially all or a part of the delusterant substance. The quantity remaining in the rayon depends of course upon the conditions employed in the finishing operations and also depends somewhat upon the volatility of the particular substance used. Residual delusterant is, in the method according to this invention, usually harmless since the substances utilized are very mild in odor and only to add weight and to soften the handle of the rayon slightly. In general, the employment of terpene ethers derived from the lower aliphatic alcohols, methyl alcohol, for example, is preferable. These ethers are substantially completely removed in the normal course of finishing the rayon. The delusterant substances used in the practice of this invention are all in the washing and desulphurizing treatments since they improve penetration of the treating liquors.

In the method according to this invention, there may alternatively be spun a viscose solution containing a dispersed delusterant composition comprising terpene ether and an additional delustering agent. For example, the delusterant composition may comprise a mixture of one of the above mentioned terpene ethers and a refined mineral oil such as "Nujol" or other light colored or colorless liquid petroleum fraction of low volatility, the ether in quantity from about 5% to 100% of the mixture, preferably in quantity from about 10% to about 40% by weight of the mixture. The delusterant composition will be added to the viscose in such amount that the said mixture will constitute from about 0.05% to about 5% by weight of the viscose, according to the effect desired. The mixture may be dispersed directly in the viscose or, if desired, it may first be emulsified in water or dilute alkali with the aid of an emulsifying agent, for example, sulfonated castor oil, and the emulsion mixed into the viscose to form a uniform dispersion. The viscose is then spun and the thread finished as usual. The terpene ether admixed with the mineral oil prevents the spinning difficulties due to agglomerations of the mineral oil particles usually encountered with mineral oil.

The delusterant composition used in the practice of this invention may also comprise a terpene ether and an inert solid delustering agent such as a pigment. For example, the delusterant composition may comprise a mixture of the terpene ether and titanium dioxide. Tin oxide, barium sulphate, antimony oxide, etc. may be used. In such a mixture, the ether has delustering properties in itself and in addition aids in dispersing the pigment and further has the important advantage of preventing agglomeration of the pigment particles. As a result, the pigment is utilized with greater efficiency and loss is required; weakening of the filament and plugging of the spinnerettes due to pigment agglomerates are avoided.

In practicing this modification of the invention, titanium dioxide may, for example, be intruded in a ball mill with one of the herein above mentioned ethers, using relatively small quantities of the latter, for example, to the extent of about 15% to about 25% by weight of the mixture. The mixture may then be further dispersed in a dilute sodium hydroxide solution in a ball mill. The dispersion is then in convenient form for addition to a viscose solution. A larger proportion of the terpene ether may be used, in which case the pigment may be dispersed in the ether and then pasted or dispersed further in water, or preferably in a dilute sodium hydroxide solution and added to the viscose.

The delusterant composition in the method according to this invention is a convenient vehicle, for incorporation in the viscose solution of substances affecting the handle of the rayon therefrom. For example, softeners such as the esterification products of triethanolamine, castor oil fatty acids or other fatty acids may conveniently be added to the delusterant composition.

The examples following further illustrate the method in accordance with this invention by specific embodiments thereof:

**Example 1**

To a spinning charge of 1700 parts by weight of viscose solution made in the usual manner and containing 6.55% sodium hydroxide and cellulose xanthate equivalent to about 7% cellulose, was added 8.5 parts by weight of the ether of pinene and methyl alcohol made by reacting methyl alcohol with wood turpentine, whereby the methyl alcohol adds at a double bond of the pinene. The ether was added slowly in a fine stream to the viscose while agitating with a 25 guilt and the agitation continued, incorporation and addition requiring about 20 minutes. The average size of the dispersed particles or droplets of the ether was 4 microns, measured immediately after mixing and again 24 hours later.

A fixing bath was prepared by dissolving 160 parts of 85% sulphuric acid and 320 parts of sodium sulphate in 520 parts of water, all parts being by weight. Thirty gallons of coagulant were prepared for each spinnerette. The coagulant was circulated at a rate of about 1 to 1.5 liters per minutes, filtering to remove suspended sulphur. The viscose containing the dispersed additive terpene ether was spun by extrusion into the fixing bath in the usual manner, a 40 filament denier yarn being formed.

The yarn was steamed and washed free of acid by a series of water washes at 40-50° C. It was desulphurized in a circulating bath of 2% sodium sulphide at 50° C, about 15 minutes being required. The yarn was then washed free of alkali by a series of washes with water at 40-50° C, followed by a cold wash at 25° C. For example, the delusterer was bleached for 30 minutes at 25° C. In a bath containing 118 cc. of bleach solution for each 10 liters of bleaching bath, the bleach solution having been prepared by chlorinating a 2% sodium hydroxide solution to the phenolphthalein flash point. The bleaching bath was carefully kept
slightly alkaline. After bleaching, the yarn was washed free of bleach by a series of water washes at 25° C. It was then steeped for 10–15 minutes in a 0.5% hypochlorite solution at 35° C. and washed free of acid by several water washes at 50–60° C. It was then hydroextracted, whizzed, and conditioned at 65% relative humidity and 70° F.

The yarn produced in this example had an appearance slightly lower in luster than commercial "semi-dull" yarn, and was characterized by a pleasing whiteness.

Example 2

The procedure of Example 1 was followed except that a quantity of delusterant 2.5% by weight of the viscose was added and dispersed therein. In addition, the delusterant consisted of a mixture of 90% of the terpene ether used in Example 1 and 10% of the esterification product of triethanolamine and castor oil fatty acids.

The viscose containing the dispersed delusterant was spun into a 40 filament 80 denier yarn and the yarn finished as in Example 1. The yarn had a degree of luster about midway between commercial "semi-dull" and "dull" yarn, the latter being completely without luster. The yarn was soft in handle and had a pleasing whiteness.

Example 3

A delusterant composition was made by forming an emulsion of 79% of the ether of pinene and methyl alcohol prepared by reacting methyl alcohol with wood turpentine, 7.9% sodium oleate, and 13.1% water. This emulsion was mixed into viscose. A 40 filament 90 denier yarn was then spun from the viscose and the yarn finished as in Example 1. A yarn of very low luster and pleasing whiteness was obtained.

Example 4

The ether of pinene and methyl alcohol was dispersed in viscose in the manner of Example 1 except that a quantity 5% of the weight of the viscose was added. The viscose was spun into a 40 filament 85 denier yarn and the yarn finished as in Example 1. A dead white yarn, substantially lusterless, was obtained.

Example 5

A delusterant composition was prepared by mixing nine parts by weight of the additive ether of pinene and ethylene glycol, prepared by reacting the latter with wood turpentine, with one part by weight of the esterification product of triethanolamine and castor oil fatty acids. This delusterant was dispersed in viscose in the manner of Example 1, adding a quantity 2.5% by weight of the viscose. The viscose was then spun to a 40 filament 69 denier yarn and the yarn finished as in Example 1. A yarn of soft handle having a degree of luster somewhat lower than commercial semi-dull yarn and having a pleasing whiteness was obtained.

Example 6

A delusterant composition was prepared by mixing seven parts by weight of the refined mineral oil known as "Nujol" with three parts of the additive ether of pinene and methyl alcohol. This delusterant was dispersed in the manner of Example 1, adding a quantity 0.5% of the weight of the viscose. The viscose was spun into a 40 filament 85 denier yarn and the yarn finished as in Example 1. It is of interest to note that the delusterant readily dispersed to particle size such that all particles were below 6 microns and that twenty-four hours later the particle size was unchanged.

A yarn of pleasing white appearance having a luster slightly less than commercial semi-dull 10 yarn was obtained.

The yarns produced in the foregoing examples were characterized by a pleasing whiteness, in some cases a dead whiteness, as compared with the opalescence produced when rayon is delustered with either pine oil or mineral oil as in previous methods. They retain their dullness when dyed to dark shades. Low denier yarns of reduced luster are readily produced as the dispersed delusterant does not agglomerate in the viscose. Furthermore, the yarns produced in accordance with this invention are odorless.

In the method in accordance with this invention there is the further advantage that viscose containing a dispersed terpene ether retains its spinnability to a high degree, that is, low denier filaments are readily spun therefrom. It has been hereinbefore mentioned that dispersed mineral oil in viscose makes for very poor spinnability and that the use of a terpene ether with the mineral oil greatly improves the spinnability. However, using the terpene ether as the sole delusterant makes for superior spinnability even when compared to the use of oils such as pine oil. Finer filaments of delustered rayon may thus be spun than was heretofore possible.

It will be understood that the details and examples hereinbefore set forth are illustrative only, and that the invention as broadly described and claimed is in no way limited thereby.

What I claim and desire to protect by Letters Patent is:

1. A viscose spinning solution for the manufacture of rayon of low luster containing a terpene ether as a delustering agent.

2. A viscose spinning solution for the manufacture of rayon of low luster containing an additive ether of pinene and an alcohol as a delustering agent.

3. A viscose spinning solution for the manufacture of rayon of low luster containing an additive ether of pinene and an alcohol as a delustering agent.

4. A viscose spinning solution for the manufacture of rayon of low luster containing an additive ether of pinene and an alcohol as a delustering agent.

5. A viscose spinning solution for the manufacture of rayon of low luster containing a terpene ether and a refined mineral oil as delustering agents.

6. A viscose spinning solution for the manufacture of rayon of low luster containing a terpene ether and a refined mineral oil as delustering agents.

7. A viscose spinning solution for the manufacture of rayon of low luster containing an additive ether of pinene and a pigment as delustering agents.

8. A viscose spinning solution for the manufacture of rayon of low luster containing an additive ether of pinene and a pigment as delustering agents.

WALTER E. GLOOR.