## ALIEN PROPERTY CUSTODIAN

## POLARIZING BODIES

Erwin Käsemann, Klein-Machnow bel Berlin, Germany; vested in the Allen Property Custodian

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This invention relates to polarizing bodies which can be used as slip-on filters for the projection of and as polarizing spectacles for the viewing of stereoscopic films, as devices for avoiding glare from automobile head lights, as photographic filters, and for similar purposes.

In my copending application Serial No. 154,204 of July 17, 1937, I have described polarizing bodies which consist of coloured foils of colletts, such as cellulose hydrate, the said foils having 10 been subjected to a strong mechanical stretch. It is an object of the present invention further to improve the polarizing bodies disclosed in that specification.

It has now been found that filters exhibiting 15particularly good polarisation can be obtained by using coloured foils of colloids such as cellulose hydrate, the production of said foils being effected in such a manner that the band obtained on pouring out viscose is first partly congulated, preferably in a neutral salt solution, then stretched mechanically, and finally subjected to complete coagulation. Viscose can be poured on to a support, such as a drum. The support can, however, be dispensed with, for example, by 25 extruding viscose directly into the coagulation bath. The neutral salt solution may consist, for example, of an ammonium sulfate solution. By undergoing partial coagulation in this bath the viscose band is solidified to a considerable extent; it can now be removed from the base and subjected to particularly vigorous stretching. Preferably the stretching is discontinued just before the breaking point is reached. Then, the coagulation of the band which is being maintained in a stretched condition is completed in an acid bath, and further treatment and dyeing is effected in the manner familiar from the production of coloured cellulose hydrate foils. This further treatment need not necessarily be car- 40 ried out while the band is in a stretched condition, since after the complete coagulation is finished the individual particles of the colloidal material of the foil are structurally fixed to a large extent.

The foils produced and stretched according to the invention have been found to take up the dye or dyes present in the dyeing solution considerably slower than do folls produced according to usual methods. Whereas ordinary foils 50 are strongly dyed within a few seconds, the dyeing of the foils according to the invention requires up to an hour and more. Hence, it is preferred to use higher bath temperatures, sometimes boiling temperatures.

It has been found that folls with particularly good polarisation are obtained when the manufacturing and stretching process of the new folls is carried out in such a manner that the finished coloured foil undergoes a shrinkage in width amounting to one fourth to one sixth or more of the original width. Even when the shrinkage in width has not been pushed so far, useful foils are obtained. The abovementioned shrinkage in width is achieved essentially by strong mechanical stretching. The result aimed at is favoured by using as raw material cellulose with a particularly high percentage of a-cellulose (say 90 to 94 per cent), or cellulose made from cotton linters. The mode of preparation of the viscose ts also essential in producing sufficient shrinkage in width. Thus, it has been found that viscose, after being subjected to a two days' preliminary maturing process at 20°C and to a subsequent maturing process at a salt value of about 2 to 3, on partial coagulation in a neutral salt solution yields a foil exhibiting a micelle structure that is especially suitable for the subsequent stretching operation and the desired shrinkage in width.

Cellulose hydrate foils produced according to the cuprammonium process can likewise be used for the manufacture of the new filters. Here again, stretching is carried out prior to the final step of complete coagulation.

Dyes belonging to the most varied classes can be employed for dyeing the colloid foils. Particularly suitable are dyes which dye cotton direct. As examples may be named benzidine dyes such as Diamine Blue, Oxamine Green G, Diamine Fast Red, etc. The light-resisting substantive dyes known under the trade name of Sirius dyes have proved especially useful.

The dyeing of the foils is carried out in accordance with the known methods of dyeing cellulose hydrate foils, preferably after the foils have left the last of the usual baths employed in their production, sald bath being, as a rule, an aqueous bath.

When dyeing foils with certain dyes and using these coloured foils as polarizing bodies, not the whole visible spectrum of light will be polarized. This will result in the colour of the foil not being extinguished in the analyzer. In order to extinguish the whole visible spectrum, two or more foils of different colours can be superimposed for the production of the new polarizing bodies, said colours being complementary so as to give, by substraction, a homogeneous grey. Care must then be taken that the polarizing axes of the individual foils are parallel.

In lieu of superimposing several foils having different colours, foils dyed with black dyes may also be used. Substantive black dyes, as a rule, consist of mixed dyes, the single components being taken up very differently by the extremely stretched foil material according to the invention. Hence, it is preferred to apply the individual dyes that are necessary for producing a homogeneous grey, in a succession of separate baths. In this manner, particularly when the progress 10 of the dyeing operation is watched colorimetrically, it is assured that of every single component there is taken up the amount necessary to produce a homogeneous grey, said grey exhibiting uniform absorption over the whole range of the 15 spectrum.

The quantity of the dyes employed is adjusted according to the amount of residual light allowed with crossed polarizing bodies formed by using the new foils. The greater the amount of residual 20 light to be allowed, the smaller the quantity of colouring matter employed for dyeing the foils. With foils intended for eliminating glare from automobile head lights, a greater amount of residual light may generally be allowed than with 25 foils to be used in the manufacture of polarizing spectacles for viewing stereoscopic motion pictures.

After the dyeing operation is finished the foils, preferably in stretched condition, are subjected 30 to drying while being continuously moved in order to effect uniform shrinkage in width. If the foil is available as an endless band it can be moved, for example, by the pair of rollers used in the production of an endless band, as mentioned below. 35

Further it has been found that particularly effective polarizing bodies consisting of cellulose hydrate folls which, at any stage of the manufacturing process or during the whole of the manufacturing process, have been subjected to a 40 strong mechanical stretch, can be obtained by dyeing said folls with iodine.

It is particularly advantageous to effect the dyeing of the foils by treating them with hydroiodic acid. Both commercial concentrated hydrolodic acid (sp. gr. 1.7) and more or less diluted aqueous solutions of hydrolodic acid are suitable. The cellulose hydrate foils which have been mechanically strongly stretched during their manufacture, are preferably dried and then immersed in an aqueous solution of hydroiodic acid. Depending on the duration of the treatment, the coloration of the foils which is thus obtained, is a more or less homogeneous grey. Preferably the folls are dyed so strongly that they exhibit a 55 transparency of 20 to 50 per cent. With a treatment ranging from half a minute to a few minutes there are obtained polarizing foils which. when crossed, transmit an extremely low amount of residual light.

In lieu of concentrated or aqueous solutions of hydroiodic acid, gaseous hydrogen iodide can be employed for dyeing the folls, the vapour of hydrogen iodide being preferably caused to act upon the damp folls which have previously been 65 strongly stretched. Other inorganic or organic compounds than hydroiodic acid, which are able to split off hydrogen iodide, may be used for dyeing.

It is to be noted that cellulose hydrate foils 70 treated with hydroiodic acid exhibit a particularly strong shrinkage in width in the direction at right angles to that of the oriented individual colloid particles of the cellulose hydrate foils. A narrow double lattice is thus formed which, on 75

the one hand, consists of the oriented, more or less transparent individual colloid particles of the cellulose hydrate foils and, on the other hand, of opaque dye particles formed by the iodine obtained from the hydroiodic acid.

It may be advantageous, during or after the treatment of the cellulose hydrate foils with hydroiodic acid, to cause mild oxidizing agents such as quinone, ferric salts, or the like, to act upon the foils.

Since iodine is volatile to a certain extent, it is preferred, after the treatment with hydrolodic acid, to coat the foils with a protective layer which renders them non-porous. As materials which have proved suitable, cellulose nitrate, cellulose acetate, celluloid, colourless synthetic resins, and similar substances, may be named. The foils treated with hydrolodic acid, after the latter has taken effect, are soaked in water for a short time, dried, and immersed in solutions of the abovementioned materials in organic solvents, such as solutions of cellulose nitrate in acetone, amyl acetate, or the like, or sprinkled with the said solutions.

The coating of the cellulose hydrate foils with protective layers which render the foils non-porous, is to be preferred not only with foils dyed by means of hydroiodic acid, but also quite generally with foils that have been dyed with inorganic or organic dyes exhibiting a certain volatility.

It has been known to impart dichroitic properties to certain colloidal organic substances by dyeing them with zinc chloride iodine solution. Apart from the fact that, on the basis of this observation, the manufacture of polarizing bodies suitable for technical purposes was not rendered possible, the polarizing properties of cellulose hydrate folls dyed by means of hydroiodic acid are considerably superior to those of foils dyed with zinc chloride iodine solution.

Polarizing bodies having particularly valuable polarizing properties and an especially high transparency can be obtained by dyeing, substan-45 tially, only the surface layers of the foils. In order to achieve the said dyeing of the surface, care must be taken to prevent the foils from swelling during the dyeing operation; similarly, folls which are strongly swollen should not be used for dyeing. Hence, during the dyeing of the foils and the operations immediately preceding the dyeing, the addition of swelling agents, such as alkalis or other substances or salts having an alkaline reaction, should be avoided. Furthermore, it is an advantage to subject the foils immediately prior to or, if desired, during the dyeing operation to a treatment with astringents such as strong acids, e. g., hydrolodic acid, acid metal salts, e. g., alums, tannin, formaldehyde, or the like. Since foils which have been mechanically strongly stretched, show less tendency to swell than do normal foils, it is preferred to carry out the dyeing not till after the stretching has been effected. By means of microtomical sections it can be readily ascertained how deep the dye from the surface has penetrated into the foil. By following the directions given above, while adjusting the length of the treatment, the concentration of the dyes, and the temperature of the baths, a coloration can be obtained which is substantially limited to the surface.

Other substances than the dyes mentioned above, such as iodine, selenium, bismuth, tellurium, etc., can be employed for dyeing the foils.

In contradistinction to the customary methods

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of dyeing with substantive dyes, these dyes are applied without the addition of swelling agents, particularly of salts.

The dyeing with iodine, as described above, is carried out by using hydroiodic acid, while the dyeing with metals or metalloids, respectively, such as bismuth, selenium, tellurium, is effected by reduction of their oxyacids by means of hydrazine hydrate or its salts. It is essential to to allow them to act only shortly on the foils to be dyed. If, when using the acids at a high concentration, e. g., at a concentration nearing saturation, the said acids are not taken up in sufficient quantity, it is prefered to cause the foils 15 to swell slightly by immersing them in water. The addition of swelling agents having an alkaline reaction should, however, be avoided. The slightly swollen foils are then immersed in the concentrated acid solutions which results in the 20 acids penetrating substantially by diffusion, while the depth of penetration is determined by the time required for diffusion. It is not till then that the foils are transferred into the solutions containing the reducing agents, when the colouring substances are precipitated.

In the production of the polarizing bodies according to the invention it has become apparent that foils made in the shape of an endless band can be stretched to a particularly high degree, the risk of breaking being smaller than in the case of bands in long lengths. The endless band is formed by pouring viscose on to the surface of a drum. The drum carrying the viscose is then transferred into a neutral salt solution, where- 35 upon the partly coagulated viscose layer is detached from the drum and placed round two rollers which rotate in the same direction and whose distance, by means of a stretching device, can be

continuously increased. The stretching of the foil is then effected by operating the stretching device. Further particulars of the manufacture of the endless band are disclosed in my copending application Serial No. 154,204.

Other colloidal organic substances than cellulose hydrate, whose molecules or micelles are oriented and which show optical properties similar to those of cellulose hydrate foils, i. e., act as employ these acids at a high concentration and 10 uniaxial crystals and rotate the plane of polarized light, can be used for the production of the new polarizing bodies. For example, as further colloidal substances there may be mentioned cellulose esters, particularly cellulose acetate. With these substances, there is first produced, by thermal or chemical means, a certain preliminary solidification of the poured or extruded foils which are then subjected to mechanical stretching, whereupon final solidification is effected.

It is preferred to employ, for the improved polarizing bodies according to the invention, foils of a thickness of <0.02 mm. Foils having a thickness of 0.005 mm have proved particularly advantageous. For this purpose, viscose is poured on to a support in a thickness of 0.25 to 0.3 mm.

The polarizing foils according to the invention, after having been coated with a protective layer. preferably after a layer of Canada balsam or a similar material has been applied to the foils, are enclosed between protective glass plates. It is preferred to employ glass having a high absorption capacity for rays of short wave length, i. e., ultraviolet rays, for example, lead glass.

The polarizing bodies according to the invention exhibit particularly desirable polarizing properties. They are optically completely homogeneous and show neither streaks nor stains.

ERWIN KÄSEMANN.