

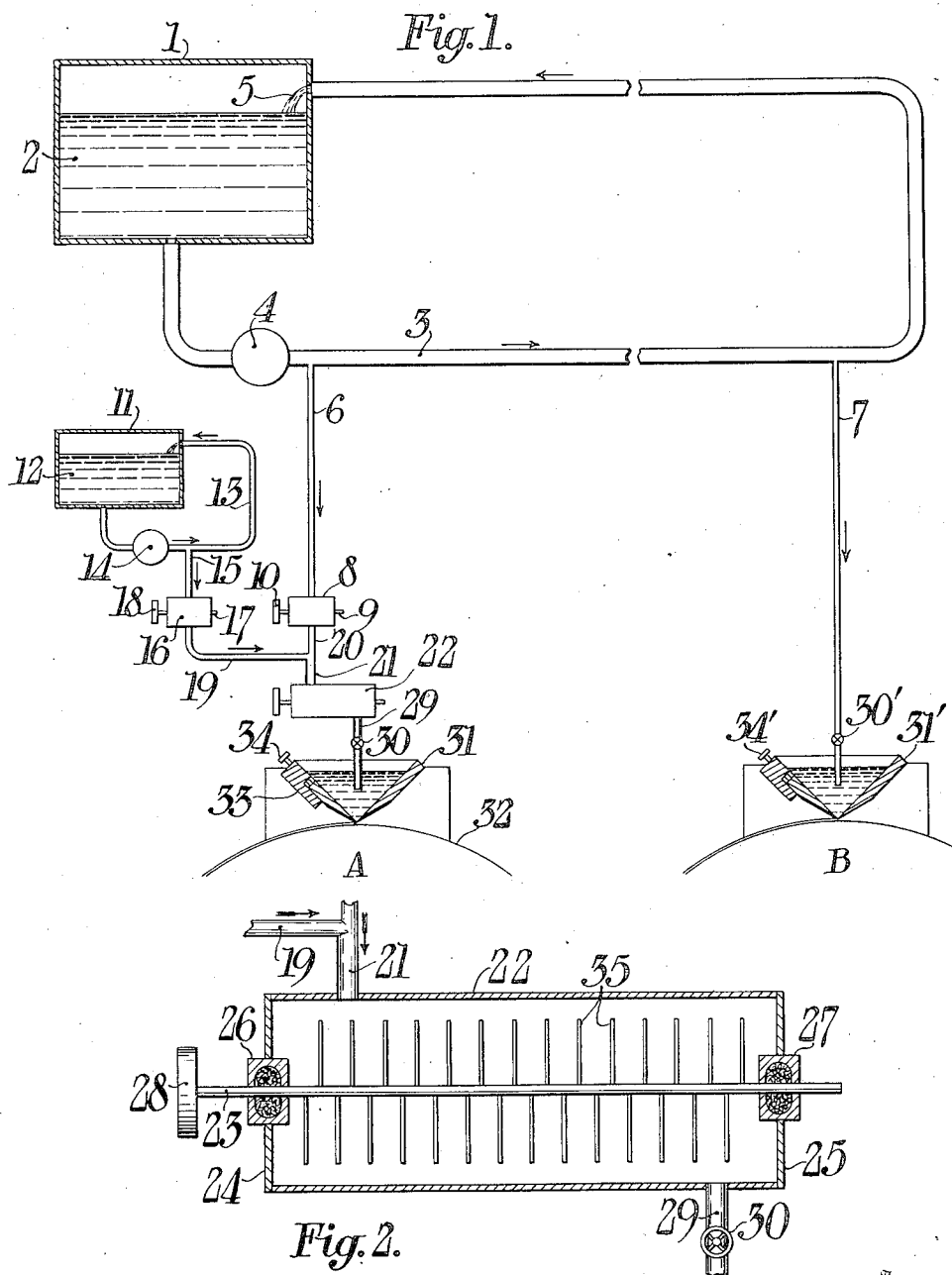
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COLORING OF CELLULOSIC SOLUTIONS

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COLORING OF CELLULOSIC SOLUTIONS

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This invention relates to a process of coloring cellulosic solutions and more particularly to a process for coloring clear solutions or dopes comprising cellulose esters dissolved in appropriate solvents.

In the manufacture of film, thin sheeting, and artificial silk it has sometimes been the practice to color such products by mixing the desired coloring material with the cellulosic solution or dope to be employed. Taking the manufacture of tinted photographic film or thin sheeting as an example, the colored solution or dope is led through the various machines where it is coated or cast into the form of sheets. If it is desired to change from one color to another, it is necessary to interrupt the whole coating operation, thoroughly clean out the storage tanks, supply lines, and casting machines at a cost of many hundreds of dollars and then make up an entirely new batch of dope of the desired color. Such methods are extremely wasteful and expensive.

The principal object of the present invention is to eliminate such wasteful methods and to provide a process wherein clear cellulose ester solutions may be colored or tinted to the desired degree without the necessity of making up an entirely new batch of the material for every color it is desired to use. Another object is to provide a method of coloring cellulose derivative solutions, and films and sheeting produced therefrom. A further object is to provide a means for coloring the cellulose derivative solutions or dopes employed in the manufacture of artificial silk. Other objects will hereinafter appear.

These objects are accomplished by the following invention which, in its broadest aspect, comprises injecting into a moving stream of clear cellulose ester solution or dope a highly colored solution, preferably of the same cellulose ester, in such a way that the desired color or tint will be produced in the clear dope. Ordinarily in the production of photographic film base and cellulose ester thin sheeting, for example, it is customary to make up a relatively large batch of dope which is kept in storage tanks and circulated to the various casting machines through supply lines or dope mains. The dope from the circulating mains is led off into the hoppers of the several casting machines, the flow of dope through the take-off line into the hoppers being regulated by a valve which supplies the material only as fast as it is consumed by the machine. In producing colored film base or thin sheeting according to known methods large batches of dope of the desired colors must be made up sepa-

rately and employed in the casting operation according to the color sheeting it is desired to produce. When it is necessary to change from one color to another the entire system including dope lines and take-offs to the respective machines have to be cleaned. As previously explained, this wastes a great deal of material besides holding up production.

In contradistinction to such wasteful and inconvenient methods, according to the present invention only clear, uncolored dopes are employed in the main circulating lines, the take-off for each machine being connected with a proportioning or metering pump. A dope of highly concentrated color is prepared and maintained in a separate storage. This highly colored dope is fed by an appropriate conduit to a second proportioning pump. The clear dope pump and the colored dope pump will then feed simultaneously to a single mixer in such proportions as to give the desired color to the final dope which is eventually fed to the casting machine. It will be evident according to this method that the clear dope in the main line is at all times uncontaminated with color, only a small quantity of the colored dope is required to be made up and kept in storage, and only a small part of the system need be cleaned when it is desired to change colors. A separate storage of concentrated colored dope may be provided for each machine or if desired a central storage tank of this concentrated colored dope may supply a number of machines with the same color of dope.

Our invention comprises broadly the coloring of clear cellulosic solutions by injecting a highly colored solution or suspension of a dye or other coloring material into a moving stream of the clear dope.

In the following description the invention will be described with particular reference to the manufacture of colored photographic film base and thin sheeting, but it is to be understood that these applications of the invention are merely typical and that the process may be applied equally well to the manufacture of a variety of products produced from cellulose ester solutions. The production of colored artificial silk by coloring a clear spinning dope is only one of the many other commercial applications of which the invention is capable.

We will now describe one example of a suitable apparatus in which the invention may be carried out in practice. Referring now to the drawing in which like numerals indicate like parts,

Figure 1 is a diagrammatic elevational view, partly in section, of a dope circulating system provided with means according to the invention for coloring the clear dope.

5 Figure 2 is a sectional elevational view of the mixing cylinder and its internal mechanism.

Referring now to Fig. 1, the numeral 1 designates a storage tank for holding the clear dope 2. This dope is drawn out into the circulating main 3 and maintained in circulation therein by means of the pump 4, any unused dope returning to the storage tank 1 by means of inlet 5.

The main circulating line is provided with take-offs 6 and 7 which convey the dope to the various machines. As shown in the drawing, take-off 6 conducts the dope through a metering pump 8 which may be of any conventional type, for example, a pump which is supplied with power by a shaft 9 driven at a constant speed by means of pulley 10 connected to a suitable source of power (not shown) and delivering a measured quantity of dope per unit time.

The numeral 11 indicates a storage tank for containing the highly concentrated colored cellulose ester dope 12 which may in some cases consist of a dye or other coloring material dissolved or dispersed in a suitable solvent. This colored dope is circulated through line 13 by means of circulating pump 14. Line 13 is provided with a take-off 15 through which the colored dope is fed through a second metering pump 16 of similar construction and operation to pump 8 referred to in the previous paragraph. This second metering pump is also operated by means of a shaft 17 provided with pulley 18 driven at a constant speed by a suitable source of power not shown.

After the metered amounts of colored and clear dope leave the metering pumps they are forced through conduits 19 and 20 respectively, these clear and colored dopes mingling in the lower enlarged portion 21 of the clear dope conduit 20. After thus mingling, the dopes enter the mixing cylinder 22 which is provided with means for vigorously agitating and mixing the clear and colored solutions, this means preferably taking the form of a rotating shaft 23 centrally disposed within the cylinder as shown in Fig. 2, passing through the cylinder heads 24 and 25, and through stuffing boxes 26 and 27 respectively. The mixture completely fills the cylinder and is preferably maintained under pressure. This prevents the formation of bubbles in the dope and causes it to emerge from the cylinder in a clear, continuous stream in condition for immediate casting. The shaft 23 is driven by means of pulley 28 rotated by a suitable source of power not shown. This centrally disposed shaft is provided within the mixing cylinder with pins 35 fixed in the shaft at right angles thereto and spaced at intervals one from another. It will be evident that the mixing may if desired, be carried out by merely injecting the highly colored dope into a moving stream of the clear dope and mixing or agitating without maintaining the mixture under pressure. In some case, as in the production of products having a streaked or striated appearance, the clear and the colored dopes may simply be run together and allowed to flow to the point of consumption.

The cylinder 22 is also provided with a delivery conduit 29 having disposed at or near its lower end a valve 30 for controlling the flow of material from the cylinder as well as for regulating the pressure therein.

Referring again to Fig. 1, the pipe 29 delivers the colored fluid into the hopper 31 from which it is supplied to the casting roll 32 in any desired thickness, the thickness of the coating being controlled by adjustment of the gate 33 operated by means of adjusting screw 34.

In the drawing we have shown a system wherein colored and clear sheeting or film base may be produced at the same time, machine A of Fig. 1 producing a colored sheet, while machine B produces a clear sheet. It will be noted that the take-off line 7 delivers a clear dope to the hopper 31 of machine B.

The above description of one type of apparatus suitable for the practice of our invention, as well as the following description of typical clear and colored dopes, is included merely for purposes of illustration and not as a limitation of our invention, as it will be evident that many changes may be made in the means and method described without departing from the spirit and scope thereof.

For example, the various pumps employed may be any of the conventional types suitable for circulating viscous fluids through a piping system. The metering pumps may be of any convenient and conventional type, such as gear pumps, piston pumps and the like. If piston pumps are used, the rate of delivery of the pumps may be regulated by regulating the stroke of the plunger. In case gear pumps are employed, the rate of delivery may be changed at will by changing the speed with which they are driven, or the actual internal capacity of the pumps. This may be accomplished by driving the pump from shafts having different speeds of rotation or from a single shaft by appropriate gear trains.

The following is an example of a coloring operation carried out in accordance with the principles of our invention.

Example 1.—A highly colored dope is prepared by dissolving 5.75 pounds of a dye sold under the trade name of Zapon fast yellow GR and 1.44 pounds of the dye sold under the trade name Zapon fast orange G in 90 pounds of acetone and then thoroughly mixing this acetone dye solution with about 194 pounds of a clear solution comprising one part by weight of cellulose acetate and 0.3 parts of diethylphthalate dissolved in 4 parts of acetone. This highly colored solution is supplied to the colored dope storage tank 11 of Fig. 1, forced by pump 14 through conduit 15 into metering pump 16 from which it is delivered through conduit 19 in a measured amount into the mixing cylinder 22, where it meets a metered amount of clear dope delivered by metering pump 8.

A clear dope composed of one part by weight of cellulose acetate and 0.35 parts of diethylphthalate dissolved in 4 parts of acetone stored in tank 1 is forced by pump 4, through take-off 6 to metering pump 8 from which it is delivered in measured quantity into the conduit 20. The colored and clear dopes meet and run together at the junction of conduits 19 and 20 and finally enter the mixing cylinder 22. The speeds of the respective metering pumps 16 and 8 are so adjusted that approximately 3 parts by weight of colored dope are fed to the mixer for every 2 parts of clear dope. The colored and clear dopes are thoroughly mixed as they progress through the mixing cylinder, the rapid rotation of the shaft causing the pins 35 to uniformly distribute the dye throughout the mass of dope. The colored dope is then forced through conduit 29, 75

past valve 30 to the hopper of the casting machine from which it is drawn and deposited on surface of the casting drum 32. After evaporation of solvents a uniformly colored sheet or film results.

Example 2.—A saturated solution is prepared by dissolving Oil Red O in acetone. This dye solution is fed to the mixing cylinder 22 where it is mixed with a dope containing one part by weight of cellulose acetate and .15 parts of triphenylphosphate dissolved in 4 parts of acetone. The outputs of the metering pumps are so regulated that one part by weight of the dye solution is delivered to the mixing cylinder for every 5 parts of the clear dope solution.

The colored dope is then run into the hopper of the casting machine as in the previous example and the desired colored sheet cast therefrom.

Example 3.—A highly colored dope is prepared by dissolving one part by weight Oil Red O and one part of Oil Scarlet 6-G in 100 parts of acetone. One part by weight of this solution is mixed with two parts of a dope made up by dissolving one part of cellulose acetate and $\frac{1}{3}$ part diethylphthalate in 4 parts of acetone. The resulting highly colored dope is injected into a moving stream of clear dope of the same composition as the clear dope of Example 2, in the ratio of one part of colored dope to 8 parts of clear dope. The resulting mixture is thoroughly mixed to distribute the color uniformly therethrough and the colored dope is then in condition for use in casting colored sheets, films and the like.

It will of course be understood that the amount of dye or other coloring material employed may be varied in accordance with the depths of color or tint desired in the finished product.

While the above examples refer to the coloring of cellulose acetate clear dopes, our invention is equally applicable to the coloring of dopes obtained by dissolving other cellulose esters in appropriate solvents or solvent combinations. It is, for example, applicable to the coloring of cellulose nitrate solutions or solutions of cellulose organic esters other than cellulose acetate, such as cellulose propionate, cellulose butyrate, cellulose stearate, or the mixed cellulose organic esters, such as cellulose acetate propionate, cellulose acetate butyrate, cellulose acetate stearate, and the like.

While the composition of the various dopes is, in general, not critical, it is preferable when coloring a clear dope to employ only solutions of the same cellulose ester in the clear and color dope solutions. For example, when coloring a clear cellulose acetate dope, it is preferable to employ a highly colored dope comprising a solution of cellulose acetate. This is primarily because of the fact that all of the cellulose esters are not soluble in the same solvents or solvent combinations.

While we have found it desirable to employ a highly colored solution of a cellulose ester as the coloring medium, it will be apparent from the Examples 2 and 3 that the dye or other coloring matter may be introduced into the clear dope and uniformly distributed therein simply in the form of a solution of the dye in an appropriate solvent without the use of cellulose esters.

While we have illustrated our method of coloring clear dope by reference to solutions of dyes only, it is also applicable to the coloring or tinting of solutions of cellulose esters by mixing therewith solutions, suspensions or dispersions of

finely ground pigment or other coloring material.

It may be said that many of the well known dyes may be employed with cellulose ester solutions, the primary consideration governing the use of these dyes being their solubility in the solvents or solvent combinations employed for making up the colored ester solution or dope. Suitable dyes for use in making up concentrated colored cellulose acetate dopes for example, are Rhodamine B, Crystal Violet, and Spirit Nitrosine R. Many other appropriate dyes and pigments will occur to those skilled in the art.

We have found it convenient to illustrate our invention by reference to the manufacture of film or thin sheeting, but it is not to be understood that our invention is limited to such processes, for it is equally applicable to the coloring of cellulose ester solutions or dope employed for any purposes for which these materials are suitable. One example of such processes is the production of colored artificial silk. In the manufacture of artificial silk a dope of the desired composition is circulated through mains and led by take-offs to the various spinning cabinets employed. It will be evident that one or a number of such spinning cabinets may be provided with means according to our invention for the coloring of the clear dope or spinning solution before it reaches the spinneret. The same advantages flowing from the use of our invention in the manufacture of film or sheeting will be present to an even greater degree in the manufacture of artificial silk due to the much greater number and complexity of the machines employed for the manufacture of this product.

It will be apparent that the present invention represents a distinct advance in the art of manufacturing films, sheeting, artificial silk and the like in that it has solved the long standing problem of providing a means of producing colored products without necessitating a shut-down of major portions of the equipment in order to change from one color to another or to employ a plurality of colors.

As many apparently widely different embodiments of this invention may be made without departing from the spirit thereof, it is to be understood that we do not limit ourselves to the foregoing examples or descriptions except as indicated in the following patent claims.

What we claim and desire to secure by Letters Patent of the United States is:

1. The continuous process of making colored attenuated articles which comprises causing metered amounts of a clear flowable cellulose ester dope and a cellulose ester dope containing a high concentration of color continuously to flow together in a definite ratio and to flow through and fill a closed space, vigorously agitating the mixture as it passes through the closed space, and thereupon forming an attenuated article from the mixed dope at approximately the rate at which it is mixed, and coagulating the formed article.

2. The continuous process of making colored sheets which comprises causing metered amounts of a clear flowable cellulose ester dope and a flowable cellulose ester dope containing a high concentration of color continuously to flow together in a definite ratio and to flow through and fill a closed space, vigorously agitating the mixture as it passes through the closed space, and thereupon casting a sheet from the mixed dope at approximately the rate at which it is mixed, and coagulating the sheet.

3. The continuous process of making colored

5 sheets which comprises causing metered amounts of a clear flowable cellulose ester dope and a flowable cellulose ester dope of a high tinctorial power continuously to flow together in a definite ratio and to flow through and fill a closed space, dispersing the colored dope throughout the clear dope by agitating the mixed dope with the closed

space under pressure, passing the resulting colored dope to a sheet-forming apparatus, casting a sheet from said colored dope at approximately the rate at which it is mixed, and coagulating the sheet.

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