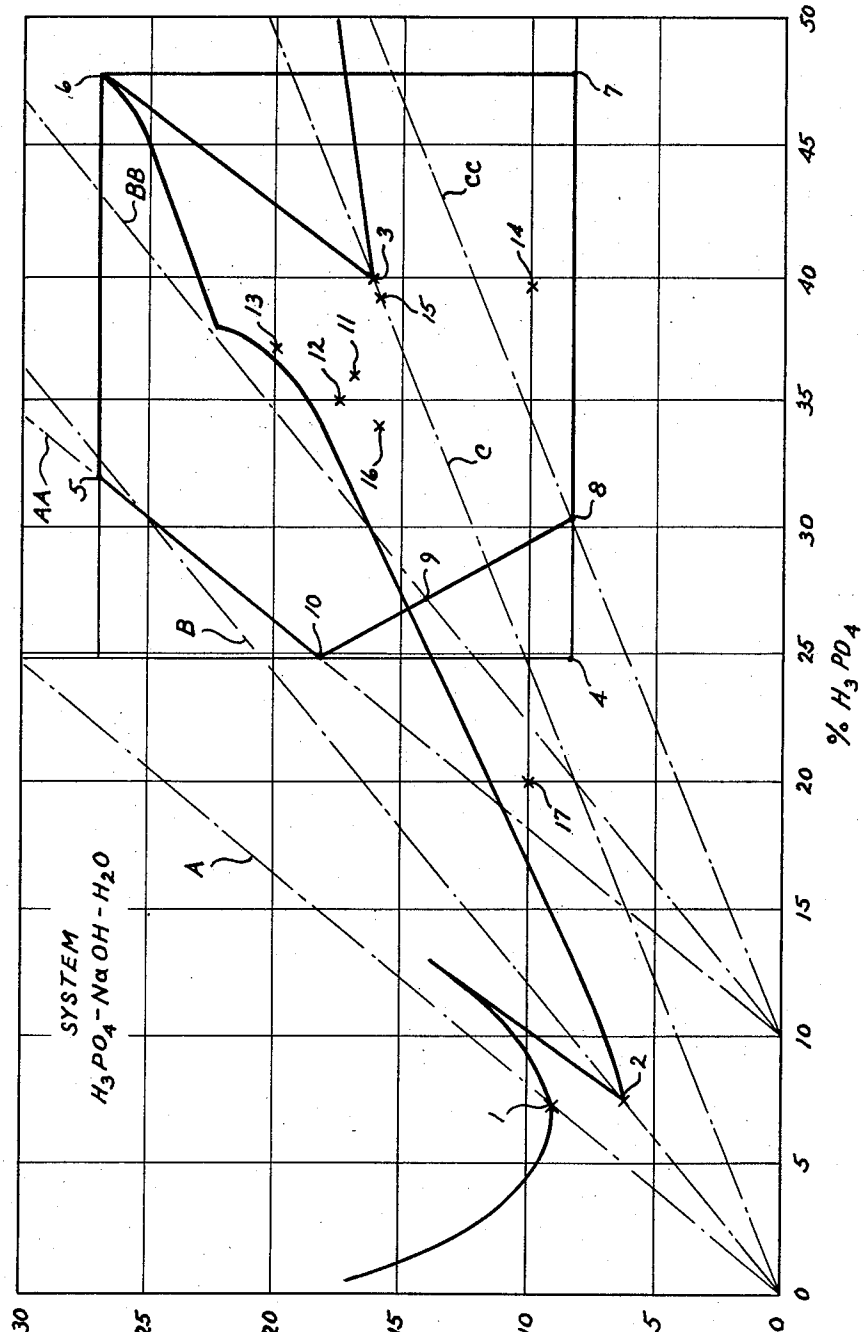
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COAGULATION OF CELLULOSIC COLLOIDS

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COAGULATION OF CELLULOSIC COLLOIDS

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This invention relates to the coagulation of hydrophilic colloids and more particularly to the coagulation or precipitation of cellulose derivatives.

Heretofore, it has been found to be impractical to use certain groups of cellulosic colloids for the formation of useful objects, such as films and filaments, because, after shaping, casting or spinning, and coagulation in the conventional or known manner, the coagulated colloids, while still in the wet gel state, were too weak and too easily torn, broken, ruptured, or punctured to be handled conveniently. While the present invention will be described in connection with cellulose derivatives such as alkali-soluble cellulose ethers of the hydroxyalkyl type, for example alkali-soluble hydroxyethyl cellulose, this is merely illustrative and not limitative, since the invention is also applicable to other colloidal cellulosic materials.

In the past it has always been found to be practically impossible to cast or spin a solution of an alkali-soluble hydroxyalkyl cellulose ether into a film of sufficient strength while in the wet gel state to permit handling on a conventional cellophane machine without xanthation of the ether before casting or without mixing the ether solution with another colloid, such as viscose and the like.

Accordingly, it is a principal object of this invention to provide a method for the coagulation of cellulosic colloidal materials so that they will have improved properties while still in the wet gel state.

Another object of the invention is to employ an improved bath for the coagulation of the cellulosic colloidal materials.

Another object of the present invention is to employ an alkaline solution of an alkali-soluble hydroxyalkyl cellulose ether having present the minimum amount of alkali to improve the properties of the coagulated ether aforesaid while still in the wet gel state.

Other objects of the invention will appear hereinafter.

Typical of baths commonly recommended for coagulating colloids of the type set out above is one composed of 5% sulphuric acid, 10% sodium sulfate and 85% water. The "standard," hereinafter referred to, refers to films coagulated by immersion in a bath of the above composition. When alkali-soluble hydroxyalkyl cellulose ethers are coagulated in such a bath, the resultant films, while in the wet gel state, are weak and subject to tearing and puncturing, and as a result incapable of being cast or formed on a conventional film-forming machine, such as that employed in the manufacture of cellophane.

The objects of the present invention are accomplished and the disadvantages of prior attempted practice as enumerated hereinbefore are overcome by employing a coagulating bath containing large amounts or relatively high amounts or proportions of the phosphate radical or

phosphate ion ($PO_4\equiv$) and an alkali metal radical such as the sodium radical or sodium ion (Na^+). The phosphate radical is present in an amount at least about 2.5 gram-moles per kilogram of solution or corresponds to a phosphate content of at least about 24.9% calculated as phosphoric acid. The alkali metal such as the sodium radical is present in an amount at least about 2.1 gram-moles per kilogram of solution or corresponds to an alkali metal content of at least about 8.3% calculated as sodium hydroxide. The pH of the coagulating bath may vary from about 1 to 8.

The bath may be formed from an alkali metal salt or salts such as a sodium salt or sodium salts of phosphoric acid or their hydrates with or without added phosphoric acid in relatively high amounts or proportions. The amounts may be sufficient so as to produce a nearly saturated solution at a temperature of 25° C. or greater concentrations may be employed by elevating the temperature of the bath.

Alternatively, the bath may be formed from phosphoric acid and the alkali metal hydroxide such as sodium hydroxide and the amount of phosphoric acid and alkali metal hydroxide may vary above the aforementioned limits.

The drawing illustrates the phase diagram of the system phosphoric acid-sodium hydroxide-water, the irregular curve representing the solubility at a temperature of 25° C. Oblique lines A, B and C represent the compositions $3NaOH:1H_3PO_4$, $2NaOH:1H_3PO_4$ and $1NaOH:1H_3PO_4$, respectively. Oblique lines AA, BB and CC represent the compositions $3NaOH:1H_3PO_4$ plus 10% H_3PO_4, $2NaOH:1H_3PO_4$ plus 10% H_3PO_4 and $1NaOH:1H_3PO_4$ plus 10% H_3PO_4, respectively.

Point 1 on the graph represents the limit of solubility of tribasic sodium phosphate at 25° C. and expresses the composition of a saturated solution in terms of the amount of sodium hydroxide and phosphoric acid present. Similarly, points 2 and 3 represent the limit of solubility of dibasic sodium phosphate and monobasic sodium phosphate, respectively, at 25° C. As will be pointed out hereinafter, it is not merely a matter of the degree of saturation of the specific bath but rather the amounts or proportions of the alkali metal and phosphate radicals present in the bath which accomplish the purposes of this invention.

The lower limit of the compositions of the baths satisfactory for the purposes of this invention is represented by the point 4 of the graph. The preferred compositions of the coagulating baths comprise solutions corresponding to at least 25% of an alkali metal salt or a mixture of alkali metal salts of phosphoric acid and at least 10% phosphoric acid. The points 8, 9 and 10 represent the compositions of baths formed from 10% phosphoric acid plus 25% of monobasic, dibasic and tribasic sodium phosphates, respectively. Thus, the preferred bath compositions lie within the pentangular area 5, 6, 7, 8, 9, 10 and 5 and may be considered as being formed from 10% phosphoric acid and at least 25% salt selected from the group consisting of monobasic, dibasic and tribasic sodium phosphates, mixtures of monobasic and dibasic sodium phosphates, and mixtures of dibasic and tribasic sodium phosphates. The preferred upper limit of compositions of the baths contain about 4.9 gram-moles of the phosphate radical and about 6.75 gram-moles of the alkali metal radical per kilogram of solution, corresponding to about 47.8% calculated as phosphoric acid and

about 27% calculated as sodium hydroxide, as represented by point 6 of the graph.

Where the composition of the bath, above the lower limit, lies beneath line C and above line 4, 7 the phosphate and sodium radicals will be present as monobasic sodium phosphate and free phosphoric acid. Where the relative proportions of sodium and phosphate radicals are such that the compositions fall on line C, the radicals will be present as monobasic sodium phosphate. Compositions between line C and line B will consist of a mixture of monobasic sodium phosphate and dibasic sodium phosphate. Compositions falling along line B will consist of dibasic sodium phosphate. Compositions lying above line B will consist of a mixture of dibasic sodium phosphate and tribasic sodium phosphate.

The use of a coagulating bath having a composition above the specified low limit results in the production of films having superior strength, clarity, elongation and the like particularly in the wet gel state. The characteristics of the films are dependent upon the proportions or amounts of the alkali metal and phosphate radicals contained in the coagulating bath. Coagulating solutions having compositions outside the specified range do not produce products having the superior properties contemplated by the present invention. The physical properties of products formed by the use of coagulating baths having compositions outside the specified range are of the order of or lower than the physical properties of products obtained by the use of the standard type coagulating baths.

The coagulation media described and contemplated by this invention are particularly effective for the coagulation of hydrophilic cellulosic colloids among which, in addition to alkali-soluble hydroxyalkyl cellulose ethers, may be named aqueous alkaline dispersions of degraded cellulose, cellulose ethers (other than those aforenamed), cellulose xanthates, cellulose ether-xanthates in dilute caustic soda, cuprammonium cellulose and the like. They are also effective for the coagulation of mixtures of such colloids.

In the practice of the present invention, alkali cellulose is made from a starting material such as wood pulp, cotton linters, etc., as by steeping in caustic soda, pressing to an approximately 2.5 or 3 to 1 ratio of alkali cellulose to original air-dry cellulose, shredding in a Werner-Pfleiderer mixer, for example, and then aging in covered cans at constant temperature and humidity. The aging process of the alkali cellulose or the degradation process is regulated carefully since the degree of polymerization of the alkali cellulose is determinative of the final viscosity of the cellulose ether solution. The aged alkali cellulose is placed in a Werner-Pfleiderer mixer and sufficient etherifying agent is added with mixing so as to introduce approximately the equivalent of 0.05 to 0.5 substituent ether groups into the final product. Any of the usual etherifying agents employed in the art are suitable in this connection. The alkali-soluble cellulose ether so produced is then dissolved in sodium hydroxide of from 2% to 10% strength. The concentration of the ether may vary from 2% to 10% depending on the degree of polymerization of the particular ether used and hence the resultant viscosity of the alkaline solution. It may be necessary in some instances, in order to produce a gel- and fiber-free solution, to lower the temperature of the same to -10.0 to $+10.0°$ C.

The solution prepared as outlined above, is filtered and deaerated with the usual equipment employed in making viscose for the manufacture of cellophane. The alkali-soluble ether solution is then forced under pressure through an elongated slit into the coagulating bath, the slit opening being such as to produce a final film having a thickness in the range from 0.0002 to 0.0150 inch. The film is coagulated and washed, by passing it through successive baths, and then dried in a manner as is cellophane. If desired, the film may be plasticized just prior to drying with the same plasticizers that are employed with regenerated cellulose film and in the same manner such as with glycerol, glycol, etc.

Sheets or films may be formed or cast by spreading the alkaline solution of the alkali-soluble cellulose ether on a casting surface, such as that of a stationary or moving plate, rotating drum, or traveling belt, which surface may be of any suitable material, such as stainless steel, Monel metal, nickel, glass or any material which is resistant to acid and alkali, to the desired thickness, or depth, immersing the same in the coagulating bath, removing the film from the casting surface, then washing and drying the same. Film may also be formed by extruding the alkaline solution of the alkali-soluble cellulose ether under pressure through a slit or die directly into the coagulating bath and removing the film therefrom by means of positively driven rolls or the like.

Films produced by the above outlined means possess increased toughness, puncture and tear resistance, clearness and improved tensile strength and elongation, especially when the film is still in the wet gel state. The films, while still in the wet gel state, show an increased ratio of colloid to solvent. The improvement in the films is due to the coagulant employed as will hereinafter be more specifically pointed out.

It is to be understood that the same marked improvements, as outlined above, are also noted when the solution is cast in the form of tubes or tubing, filaments, yarns, fibers and other like shaped objects.

In order to more specifically explain the nature of the present invention, the following examples are set forth. But it is to be understood that these examples are merely illustrative and the invention is not intended to be limited thereby.

EXAMPLE I

In conventional manner, i.e., by extrusion through a die, films were cast at a thickness, or depth, of 0.015 in. from a composition comprising 6 parts of alkali-soluble, water-insoluble hydroxyethyl cellulose, 8 parts of NaOH and 86 parts of water. Before use, this composition was filtered and deaerated. The hydroxyethyl cellulose was characterized as being insoluble in water and soluble in dilute aqueous alkalies on chilling to approximately 5° C. and as having a viscosity of 6 times that of glycerol at 25° C. when made into a composition as described above. This viscosity acts as a practical index of the degree of polymerization of the hydroxyethyl cellulose. The films were coagulated by extruding into a bath comprising an aqueous solution of 36% H_3PO_4 and 17% NaOH maintained at 25° C. The composition is represented by point 11 on the graph. The films were rinsed thoroughly in constantly changing water at 45 to 55° C. The still wet films were subjected to physical testing the results of which are tabulated below in Table 1.

For the purposes of comparison, films were cast as in Example I, from the same composition therein described, except that the films were coagulated by means of a conventional or standard bath, for example, an aqueous solution of 5% H_2SO_4 and 10% Na_2SO_4. The films were rinsed thoroughly in constantly changing water at 45 to 55° C. Films prepared in such manner will hereinafter be referred to as "standard" films. These films were characterized by cloudiness whereas films of Example I were clear. Also, the standard films were so weak that they could not be passed between squeeze rolls before plasticizing and drying such as employed on standard film casting equipment thus indicating that the standard coagulating bath is incapable of satisfactorily producing films in practical commercial operation. Example I films were capable of being passed through squeeze rolls while in the wet gel state and were far superior to standard films in this respect.

Both standard and Example I films were plasticized by immersion in 3% aqueous glycerol solution. The plasticized films were placed on frames, dried, conditioned

at 75° F. and 45% relative humidity and subjected to physical testing, the average results of which are tabulated in Table 1. The plasticized and conditioned films of Example I were clear while the similarly treated standard films were cloudy.

Table 1 [1]

Type Film	Thickness of Film Tested, inches	Tensile Strength, gms.	Percent Elongation
Still Wet:			
Standard	0.0095	245	72
Example I	0.0058	310	75
Plasticized, Condition:			
Standard	0.00121	2,060	42
Example I	0.00113	2,290	33

[1] Tests made on a standard Schopper Tester.

From the above data it can readily be seen that films produced according to the present invention are decidedly stronger than conventional or standard films, especially when wet.

It is to be understood that the term "films" as used herein is meant to include such products as casings for meats and cheese, bands for bottles, tubes, and the like, sometimes described as pellicles.

In place of the die of Example I containing an elongated slit for the production of films, there was employed a die containing a plurality of small openings, commonly known as a "spinneret," for the production of fibers, filaments and yarns. The composition, coagulating bath and procedure of Example I is generally the same and such filaments, etc., are far superior to those produced when a standard coagulating bath is employed.

EXAMPLE II

Films were cast as described in Example I from a composition as therein described and were coagulated by immersion into an aqueous bath comprising 35% H_3PO_4 and 17.5% NaOH at 25° C. The composition is represented by point 12 on the graph. This bath was nearly saturated. The films were rinsed as described in Example I and were clearer than those cast in the standard bath and were tougher, thinner, and more resistant to tearing and puncturing, these observations being made just after coagulation and rinsing.

Both Example II and standard films were immersed in an aqueous 5% glycerol solution, the usual commercial film plasticizering bath, while still in the wet gel state and were allowed to remain in this solution for a period of one week. When examined at the end of this period, the Example II films were still strong and could be removed from the solution and handled without breaking or tearing. That is to say, they still were self-sustaining films and capable of being passed between squeeze rolls before plasticizing and drying. However, when the standard films were examined, they were found to be so weak as to be incapable of removal from the solution without falling apart. That is to say, they were no longer self-sustaining films.

Another noticeable difference between Example II and standard films was the percentage of cellulosic material in the still wet rinsed films (films in the wet gel state). The films coagulated in the standard bath were 9.7% cellulosic, while those coagulated in the bath of Example II were 15.8% cellulosic showing an increase of 63% cellulose content of the latter over the former. In other words, the ratio of hydroxyethyl cellulose to water was 10.7/100 for the standard films and 18.8/100 for Example II films.

EXAMPLE III

Films were cast, as described in Example I, from an alkaline solution of a low substituted cellulose glycollic acid, the composition of said solution being the same as Example I. The sodium salt of this acid was characterized as being soluble in dilute aqueous alkalies, but insoluble in water, organic solvents, etc. Films cast in the standard bath were so weak after rinsing as to be incapable of being passed between squeeze rolls before plasticizing and drying whereas films cast in a bath as described in Example II, having a composition as represented by point 12 of the graph, could be passed between squeeze rolls in routine manner and with no special precautions. The latter films were also much stronger, tougher and more tear and puncture resistant while still wet.

EXAMPLE IV

The procedure of Example I was repeated except that an aqueous coagulating bath comprising 37% H_3PO_4 and 20% NaOH was used. The composition is represented by point 13 of the graph. The surface of the film was covered with a beautfiul "crystalline" or "frosted" design. This effect can be utilized for producing delustered rayons, filaments, staple, etc., for imparting a novel sheen to such materials, etc. Physical data were obtained and will be found in Table 2 following Example V.

EXAMPLE V

The procedure of Example I was followed except that an aqueous coagulating bath comprising 39.6% H_3PO_4 and 16.2% NaOH was used. This bath was a substantially saturated solution of NaH_2PO_4, of a composition represented by point 3 of the graph and had a pH of 3.1 at 25° C. A "crystalline" effect was obtained but not to as marked a degree as in Example IV. The still-wet films coagulated in the standard bath were 9.3% cellulosic while those coagulated in the Example V bath were 14.4% cellulosic; an increase of 55%. In other words, the ratio of hydroxyethyl cellulose to water was 10.3/100 for the films from the standard bath and 16.8/100 for films from the Example V bath. Physical data were obtained and are tabulated in Table 2.

Table 2

VARIATION IN PHYSICAL PROPERTIES OF FILMS

("Phosphate" [1] vs. "Standard")

[Based on films coagulated in standard bath.]

Type Film	Thickness of Film Tested, Percent Change	Tensile Strength, gms., Percent Change	Percent Change in Percent Elongation
"Still Wet":			
Ex. I	−39	+27	+4
Ex. IV	−36	+38	+7
Ex. V	−43	+25	−7
Plasticized, Conditioned:			
Ex. I	−7	+11	−21
Ex. IV	−9	+22	−31
Ex. V	−21	+17	−17

[1] Phosphate refers to a coagulating bath composed of H_3PO_4 and NaOH.
(+=increase and −=decrease.)

EXAMPLE VI

Films were cast as described in Example I from a composiiton comprising 7.8 parts alkali-soluble, water-insoluble hydroxyethyl cellulose, 7 parts sodium hydroxide and 85.2 parts water. The hydroxyethyl cellulose, used in this example, is characterized as having a viscosity 6 times that of glycerol at 25° C. when made into a solution comprising 6 parts of hydroxyethyl cellulose and 9 parts sodium hydroxide. The coagulating bath employed comprised an aqueous solution of 15% H_3PO_4 and 30% NaH_2PO_4. The composition of this bath corresponds to about 39.5% H_3PO_4 and 10% NaOH and is represented by point 14 of the graph. This bath has a pH of 1.2 at 25° C. The films so produced were superior to all others in clearness, toughness, were thinner and more resistant to tearing and puncturing, the observations being made just after coagulation and rinsing. The

hydroxyethyl cellulose employed in this example contained approximately the equivalent of 0.2 substituent group.

It is also to be noted that excellent tubing may be cast into a bath such as the above. This tubing is suitable for the packaging of meats, cheeses, and the like.

It is important in the above examples, from a practical standpoint, to maintain the lowest possible concentration of NaOH in the colloidal solution to maintain solubility of the alkali-soluble, hydroxyethyl cellulose. By proceeding as in Example VI excellent results have been obtained when the NaOH concentration is 5%, for certain hydroxyethyl cellulose ethers, and as low as 2% for others.

The use of the coagulating baths of this invention permits the production of sheet on conventional cellophane equipment from cellulosic colloids heretofore deemed highly impractical with the use of conventional coagulating baths. The following examples illustrate such sheet production:

EXAMPLE VII

Film was produced on a semi-commercial scale cellophane machine by continuous extrusion of a cellulose ether solution, as described in Example I, into a coagulating bath having a composition corresponding to 39% H_3PO_4 and 16% NaOH, point **15** of the graph, the temperature of the bath being maintained at 28° C. to 35° C. The film was extruded with very thin edges, was passed through wash tanks (55° C.) to rinse the sheet free of salts, was passed through a plasticizing solution, 4% glycerin solution at 55° C., and dried by passing over rolls maintained at about 80° C.

The coagulated, wet film or sheet was clear, extremely tough and resistant to tearing and puncturing and was passed through the machine without difficulty. The finished sheet was very clear, tough and possessed a high shatter resistance, high tensile strength and high stretch.

EXAMPLE VIII

Film was produced on a semi-commercial scale cellophane machine and by the use of the coagulating bath as described in Example VII. The alkali-soluble, water-insoluble hydroxyethyl cellulose, however, differed from that of the cellulose ether of Example VII in that it was characterized by being soluble in lower concentrations of caustic soda, 3% aqueous caustic soda solution, but had essentially the same viscosity when made into a solution containing 6% alkali-soluble hydroxyethyl cellulose, 9% NaOH and 85% water. The extrusion solution contained 6% hydroxyethyl cellulose, 5% NaOH and 89% water. The film was extruded as described in Example VII, was passed through wash tanks (85° C. to 95° C.) to rinse the sheet free of salts and dried by passing over rolls maintained at about 80° C. The sheet was produced without the use of a plasticizer.

The coagulated, wet film was extremely tough and comparable to the film of Example VII. The finished sheet which was unplasticized was very clear, tough and had characteristics similar to plasticized films made from viscose.

In the practice of the present invention, its objects are accomplished by the use of phosphate salt in the coagulating bath. If a salt of phosphoric acid, used in the coagulating bath, is effective for the purposes of this invention, it cannot be assumed that the acid itself or only the phosphate radical is the effective agent. For example, films were cast as in Example I except that the coagulating bath or baths consisted of aqueous H_3PO_4 varying in concentration from 5% to 75% H_3PO_4, inclusive. Still wet films and also plasticized, dried and conditioned films were examined and none of them showed any appreciable differences in properties when compared with films coagulated in the standard bath. Also, these films did not have properties comparable to films such as described in Examples I and II.

Water-soluble sodium carboxymethylcellulose does not dissolve in a solution such as the coagulating bath of Example II, namely, 35% H_3PO_4 and 17.5% NaOH. Hence a 1% aqueous solution of water-soluble sodium carboxymethylcellulose is capable of being coagulated in such a solution (Example II bath) as also is a composition comprising 6 parts of weight of water-soluble sodium carboxymethylcellulose and 100 parts of 8% aqueous caustic soda solution. The present invention can be applied to the production of films, filaments, shaped objects, etc., such as water-soluble yarns, and the same will be clear to those skilled in the art.

The present invention is also useful in coagulating the alkali-soluble hydrophilic cellulose colloids in situ in another body such as cotton batting, fabrics, fibrous webs or sheets, and the like. This is pointed out particularly by the following example.

EXAMPLE IX

A web of loose cotton batting was supported on a screen and treated with an excess of a composition comprising 1 part of hydroxyethyl cellulose characterized as in Example 1, 3 parts of NaOH, and 96 parts of water. The excess solution was allowed to drain off and the wet batting was treated with an excess of an aqueous solution comprising 34% H_3PO_4 and 16% NaOH thus coagulating the alkali-soluble hydroxyethylcellulose in situ. The composition of the bath is represented by point **16** of the graph. The impregnated cotton was rinsed thoroughly and dried. There was produced a non-woven fabric of exceptional absorbency and wet and dry strength. By means of the procedure of the present example there may be produced non-woven fabrics, bonded webs, paper suitable for wrapping rayon cakes, etc., in accord with the principles of the present invention.

The coagulants are especially useful in connection with cellulosic colloidal impregnants, saturants, coatings, sizes, binders, etc. for textiles, paper, non-woven fabrics, bonded webs, etc. Colloids, applied to textile materials and coagulated as herein proposed, exhibit increased laundry resistance, improved retention of hand, etc. With paper and bonded webs improved wet strength is noted.

Films cast from hydrophilic colloids by means of the present invention have superior properties while still wet such as increased toughness, and puncture and tear resistance, decreased brittleness, improved tensile strength and elongation, increased ratio of colloid to solvent, and increased shrinkage of shaped object at the time of coagulation. Dry films may be exceptionally clear, or may have a novel finish or surface character such as a velvet-like sheen or a crystal-like or "frosted" decorated surface. Multilayered films can be cast from more than one colloid to yield special purpose films, decorated films, tubes, etc.

The following examples illustrate the use of coagulating baths having compositions outside the specified range.

EXAMPLE X

Films were also prepared as described in Example I from a cellulose ether solution of a composition specified in Example I by utilizing a bath consisting of approximately 12.3% tribasic sodium phosphate which corresponds to 7.3% H_3PO_4 and 9% NaOH. This coagulating bath was a substantially saturated solution of tribasic sodium phosphate at 25° C. and is represented by point **1** on the graph. The physical properties of both the wet and finished films were substantially the same as the films formed in a standard bath. The films were very slightly weaker in the wet condition and slightly stronger in the dried condition as compared to films prepared by the use of a standard bath. However, the films produced from this bath were more hazy than those from the standard bath.

EXAMPLE XI

Films were cast from a composition and by the method as described in Example I utilizing a coagulating bath consisting of approximately 11% disodium phosphate corresponding to about 7.5% H_3PO_4 and 6.3% NaOH. This bath was a substantially saturated solution of dibasic sodium phosphate at 25° C. and the composition is represented by point **2** of the graph. The films produced in this bath had a crinkle or waviness in the surface and were generally inferior in their physical properties to films produced by the use of a standard coagulating bath.

It will be noted that Example V showed the use of a coagulating bath consisting of a substantially saturated solution of monobasic sodium phosphate and the baths of Examples X and XI involve the use of substantially saturated solutions of tribasic sodium phosphate and dibasic sodium phosphate respectively. Although in all three examples the sodium and the phosphate radicals may be considered as being present in a bound state as specific salts, the action of the salts is not comparable. Also, in each instance the solution consisted of a substantially saturated solution of the respective sodium salt. It is apparent that the degree of saturation of the specific bath is not a controlling element. It is clear that in this invention it is the relative amounts of the sodium and phosphate radicals which permits the attainment of the objects of this invention. This is further shown by the following example.

EXAMPLE XII

Films were cast from a cellulose ether composition and by the method described in Example I. The coagulating bath employed consisted of a solution containing 20% H_3PO_4 and 10% NaOH as represented by the point **17** on the graph. The clarity and physical properties of the films were slightly superior to those of films prepared by the use of a standard coagulating bath. The principal difference between the films was a small increase in the proportion of cellulose in the wet film formed by the use of the phosphate coagulating bath as compared to the standard bath. The films did not possess the characteristics and properties of films formed by the use of the coagulating baths of this invention.

There are a number of advantages of the present invention which are important in connection with the use of the coagulants. As the coagulants are used preferably at concentrations very near to, or at saturation, recovery is simple and relatively inexpensive since relatively small amounts of solvent need to be evaporated. The effectiveness of coagulation is increased since it takes place at relatively low temperatures which makes heating of the baths usually unnecessary and facilitates temperature control of the same. However, good results are also obtained when the temperature is varied from room temperature up to 45° or 50° C.

This application is a continuation-in-part of my copending application entitled Coagulation of Colloids, Serial No. 127,801, filed November 16, 1949, and now abandoned.

It is to be understood that the description above is merely illustrative and that changes and variations may be made without departing from the spirit and scope of the invention as defined in the appended claims.

I claim:

1. A method of producing filaments, films and tubes which are self-supporting in the wet gel state which comprises dissolving an alkali-soluble cellulosic material in an aqueous alkaline medium and extruding the resulting solution through an orifice into an aqueous coagulating bath comprising an aqueous solution consisting essentially of water, the phosphate radical in an amount of at least about 2.5 gram-moles per kilogram of solution and an alkali metal radical in an amount of at least about 2.1 gram-moles per kilogram of solution.

2. A method of producing filaments, films and tubes which are self-supporting in the wet gel state which comprises dissolving an alkali-soluble cellulosic material in an aqueous 2% to 10% sodium hydroxide solution and extruding the resulting solution through an orifice into a coagulating bath comprising an aqueous solution consisting essentially of water, the phosphate radical and an alkali metal radical and having a composition included within the limits defined by the pentangular area **5, 6, 7, 8, 9, 10** and **5** of the graph in the accompanying drawing, the amount of alkali metal being calculated as sodium hydroxide.

3. A method of producing filaments, films and tubes as defined in claim 2 wherein the alkali metal of the coagulating bath consists of sodium.

4. A method of producing filaments, films and tubes which are self-supporting in the wet gel state which comprises dissolving an alkali-soluble cellulosic material in an aqueous alkaline medium and extruding the resulting solution through an orifice into an aqueous coagulating bath comprising an aqueous solution consisting essentially of water, the phosphate and sodium radicals and having a composition corresponding to at least 10% phosphoric acid and at least 25% phosphate salt selected from the group consisting of monobasic, dibasic and tribasic sodium phosphates, mixtures of monobasic and dibasic sodium phosphates and mixtures of dibasic and tribasic sodium phosphates.

5. A method of producing filaments, films and tubes which are self-supporting in the wet gel state which comprises dissolving an alkali-soluble cellulosic material in an aqueous 2% to 10% sodium hydroxide solution and extruding the resulting solution through an orifice into a coagulating bath comprising an aqueous solution consisting essentially of water, at least 15% phosphoric acid and at least 30% monobasic sodium phosphate.

6. A method of producing filaments, films and tubes which are self-supporting in the wet gel state which comprises dissolving an alkali-soluble cellulosic material in an aqueous 2% to 10% sodium hydroxide solution and extruding the resulting solution through an orifice into a coagulating bath composed of an aqueous solution of monobasic sodium phosphate, the solution containing an amount of monobasic sodium phosphate substantially equal to that of a saturated solution at 25° C.

7. In a method of forming shaped articles of cellulosic material the step which comprises extruding a liquid containing a cellulosic material selected from the group consisting of alkali-soluble cellulose ethers, water-soluble cellulose ethers, alkaline dispersions of degraded cellulose, cellulose xanthates, cellulose ether-esters, cuprammonium cellulose and mixtures thereof into a coagulating bath comprising an aqueous solution consisting essentially of water, the phosphate radical in an amount of at least about 2.5 gram-moles per kilogram of solution, and an alkali metal radical in an amount of at least about 2.1 gram-moles per kilogram of solution.

8. The step in a method as defined in claim 7 wherein the alkali metal radical is sodium.

9. In a method of forming shaped articles of cellulosic material the step which comprises extruding a liquid containing a cellulosic material selected from the group consisting of alkali-soluble cellulose ethers, water-soluble cellulose ethers, alkaline dispersions of degraded cellulose, cellulose xanthates, cellulose ether-esters, cuprammonium cellulose and mixtures thereof into a coagulating bath comprising an aqueous solution consisting essentially of water, the phosphate radical and an alkali metal radical and having a composition included within the limits defined by the pentangular area **5, 6, 7, 8, 9, 10** and **5** of the graph in the accompanying drawing, the amount of alkali metal being calculated as sodium hydroxide.

10. The step in a method as defined in claim 9 wherein the alkali metal radical is sodium.

11. The step in a method as defined in claim 9 wherein the liquid is an aqueous solution containing between 2% and 10% sodium hydroxide, the cellulosic material is an alkali-soluble cellulose ether and the alkali metal radical in the coagulating bath is sodium.

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