June 2, 1942. E. CZAPEK 2,285,147

PROCESS OF MANUFACTURING FOILS, FILMS, AND THE LIKE

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Fig. 1.

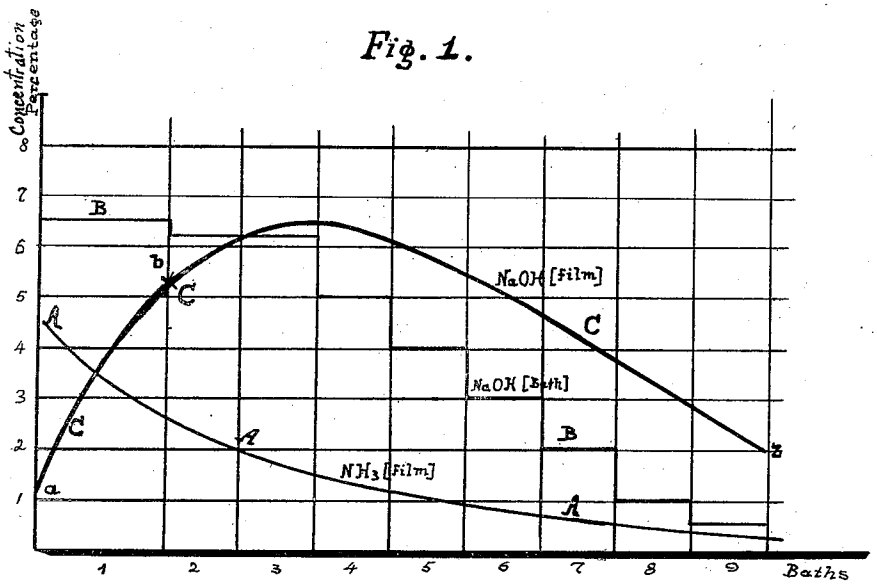
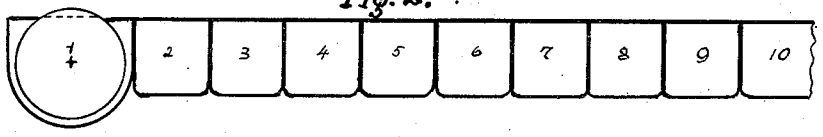


Fig. 2.



Coagulation Bath — Treatment Baths — Regeneration Bath

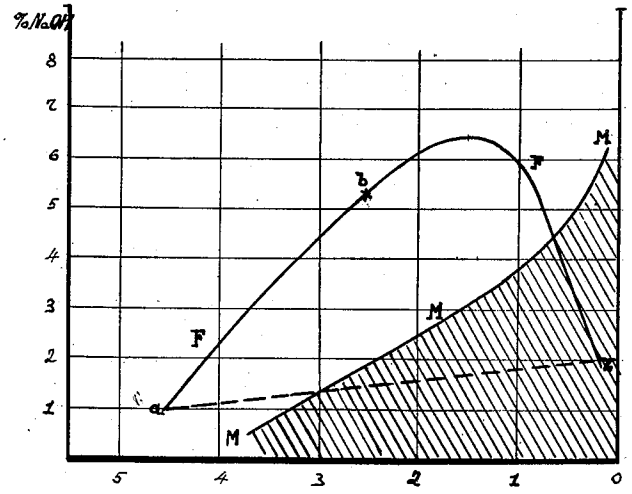


Fig. 3.

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PROCESS OF MANUFACTURING FOILS, FILMS, AND THE LIKE

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3 Claims. (Cl. 18—57)

This invention relates to processes for manufacturing foils, films and the like from solutions of cellulose in copperoxide ammonia.

Among the objects of the present invention, it is aimed to provide an improved process for manufacturing foils, films, film sheets and the like from solutions of cellulose in copperoxide ammonia, the product of which is uniform throughout in tensile strength, is free from striations, streaks and the like and free from weak spots and variations in thickness so frequently resulting from an undue tension or pull of the sheet in embryo with the processes heretofore used.

These and other features, capabilities and advantages of the improved process constituting the present invention will appear from the accompanying drawing in which

Figure 1 is a diagrammatic view showing the respective degrees of concentration of lye in the film sheet in embryo, as compared to the degrees of concentration of lye in the baths and also compared to the degrees of concentration of ammonia in the film sheet as the steps of the process succeed one another;

Fig. 2 is a diagrammatic view of a series of baths constituting graphic projections of the baths on the diagram shown in Fig. 1 and to be read in connection with Fig. 1;

Fig. 3 is a diagram showing the degrees of concentration of ammonia and lye in the film sheet as the steps of the process succeed one another.

The improved process is characterized essentially by the definite relations of different degrees of concentration of sodium hydroxide in a plurality of successive baths for effecting coagulation and treatment of the film stock to be produced. Otherwise, the steps of the process are those well known in the art consisting in spreading the cellulose solution which passes into a coagulation bath and in treating the coagulated strip after the coagulation of the solution and after effective diffusion of the coagulation liquid throughout the resulting product. The above mentioned spreading of the cellulose solution can be effected either freely and without supporting base directly into the coagulation bath or it may be effected by pouring the cellulose solution at first onto a supporting base and moving the same into the coagulation bath.

It has been found that the coagulation of cellulose solutions in copperoxide ammonia can be effected in any one of several ways according to the particular combination of coagulating liquid and cellulose solution selected either to produce a coagulated film that is soft and plastic or hard and strong. It was further found that the soft film on its way through the coagulation baths and subsequent treatment baths is exposed to changes in its structure, especially to stretchings, striations and swellings, resulting in a completed article characterized by definite imperfections. During the subsequent treatment just mentioned as an instance, a soft film might be stretched lengthways due to the stretch of the film sheet, the resistance encountered on the way, and the shrinkage caused by regeneration, in consequence of which it will shrink in a transverse direction more than otherwise necessary. This unequal extension of the film sheet in these directions will result in a finished product having weak spots and generally lacking uniformity in stability, strength and extension qualities. Since the hard film is not subjected to these objectionable influences, it will shrink only slightly in width in the coagulation and treatment baths; and an appreciable shrinkage only occurs in the regeneration bath. Furthermore, due to the hardness of the film, this shrinkage is less than is the case with soft films; and still is substantially equal in the length and transverse directions.

As essential to the formation of such hard films and to their remaining in such strong condition, after extensive study and experiment, certain characteristics leading up to the present discovery were observed.

It was observed, as an instance, if a process is characterized by the formation of a precipitate of copper hydroxide at the beginning of the coagulating treatment, and augmented in the subsequent treatments, the so formed film structure is soft throughout these treatments, and consequently during the accompanying transportation of the film structure and the resulting drawing action exercised on the film, striations, distortions, deformations and the like will result. Furthermore, if a copper hydroxide precipitate did not occur at the beginning of the coagulation treatment, but only in the subsequent treatments, the so formed film structure may have a tougher surface hardness than aforesaid, but it will not be sufficient to avoid the aforesaid striations, distortions, deformations and the like. On the other hand, if a copper hydroxide precipitate did not occur either in the preliminary coagulation or in the subsequent alkaline treatments, there will result a film structure sufficiently hard definitely to resist the ordinary internal stresses, and consequently prevent the

aforesaid deformations during these treatments. If, in this latter case, a small turbidness which entirely disappears in the final regeneration, should occur after the cleaning of the film had progressed to the point that the ammonia had been practically washed out and the film contained only a small amount of caustic soda solution, this turbidness no longer would result in the formation of striations, streaks and deformations. For instance, a solution of cellulose in copperoxide ammonia and having a content of 7 per cent cellulose and 4.5 per cent of ammonia and 3.3 percent of copperoxide introduced in a large quantity of a coagulation bath consisting of 8 per cent of sodium hydroxide, 0.6 per cent of ammonia and 91.4 per cent of water would positively prevent the forming of any copper hydroxide in the film during the coagulation. The important point, however, was that the hard coagulated film continued hard throughout the entire process until the regeneration bath was reached and that then during the short state of slight turbidness, which then occurred, it did not lose its strong characteristic.

In order to produce a strong film and in order to keep it in this condition during the subsequent treatment, according to the present invention, the coagulation of the cellulose solution on the pouring base takes place with an alkaline liquid, containing a caustic alkali, for instance sodium hydroxide, and ammonia. The concentration ratio between sodium radicals, Na, and ammonium radicals, NH_4, has to be selected, so that the sodium radicals in the bath liquid exceed the ammonium radicals, contained in the cellulose solution and in the bath liquid in order positively to prevent the forming of copper hydroxide in the film during the coagulation.

Furthermore, the ensuing treatment, in the subsequent baths is started with a comparatively high concentration of sodium radicals, Na, sufficient to exceed the ammonia radicals in the film stock being formed and in the bath liquid. Simultaneously with a progressively diminishing ammonia concentration in the film will the quantity of sodium radicals, Na, be decreased from bath to bath in the following treatments, to retain a concentration ratio between sodium and ammonium radicals, which is suitable to prevent the forming of copper hydroxide precipitate in the film while passing through the baths having decreasing alkaline contents.

The selection of the concentrations for the treatment baths vary within certain limits according to the composition of the cellulose solution, according to the thickness of the film to be produced and according to the temperature of the coagulation and the working speed. As an instance, in the manufacture of films, which in their final condition have a thickness of 0.007 to 0.12 mm., concentrations of caustic soda solution at the start from 4.5 to 11 per cent when the concentration of ammonia at the start is from 0.2 to 1.2 per cent have proven to be satisfactory for the coagulation bath.

If the process just described is followed in the steps preceding the treatment of the film in the acid bath, a comparatively hard, strong film is obtained, which does not depart from its original width and in addition shrinks only slightly in the acid bath.

Films made in accordance with this process distinguish themselves by a decided regularity or uniformity in their structure, a high stability, strength and a stretching capacity or extensibility substantially equal in the length and transverse directions.

The steps of the process now to be described of one specific example are, of course, not intended to be all inclusive but merely typical of the invention. These steps are as follows.

A solution of cellulose in copperoxide ammonia is poured onto a pouring base by which it is introduced into a coagulation liquid which contains a comparatively large quantity of sodium radicals, Na, and a comparatively small quantity of ammonium radicals, NH_4, and while supported on this base the solution is coagulated to the point where the forming strip is entirely penetrated by the coagulation liquid. This stage or condition is reached, it has been observed, when the coagulation liquid penetrates the inner part of the strip and moistens the pouring base.

It may be noted in this connection that instead of sodium hydroxide also the lye of another alkaline metal can be used. Furthermore, it is advisable, to conduct the coagulation in a flow of coagulation liquid in order to avoid the formation of concentration differences in the boundary surface during the coagulation, so that the gradient of potential between cellulose solution and coagulation bath existing and desired at the beginning may remain undisturbed as much as possible in all parts and throughout the entire width of the film sheet. This object is achieved in a particularly effective way when causing the coagulation bath liquid to move in an opposite direction to the direction of movement of the film sheet.

The so formed strip is then removed from the base and carried through several treatment baths which also contain sodium radicals, Na, besides ammonium radicals, NH_4, in various degrees of concentration as hereinafter to be described. After leaving these treatment baths, the film sheet then passes into a regeneration bath which contains diluted sulfuric acid. As soon as the film has passed the regeneration bath, it is to be washed and dried in the usual manner and dyed or impregnated with softeners respectively.

The selection of the degrees of concentration in the successive baths which have been found to meet the requirements of the present invention can be conveniently compared with the course of the process generally on a chart, see Fig. 1 where the values on the ordinate indicate the degrees of concentration of ammonia and alkali lye from 1 to 8 per cent as indicated and the values on the abscissa indicate the successive stages or successive baths from 1 to 10 as indicated through which the film stock passes during its treatment.

As an instance:

Graph A on Fig. 1 represents the degree of concentration of ammonia in the film, graph B the degree of concentration of alkali lye in each bath and graph C represents the concentration of alkali lye in the film resulting from the thus charted concentrations in the film and bath. In practice, as shown by the diagram or chart, the ensuing treatment and cleaning baths are ordinarily charged in stages by an alkali lye of gradually diminishing concentrations starting with bath 1 and continuing on to bath 9. This part of the process of course can also be carried out, starting in the reverse direction by filling the last bath anew with fresh water and conducting the water toward the preceding baths in the direction opposite to the direction of the path of movement of the film stock. In bath 9, as an in-

stance, the lye concentration then would at the very start be brought to a little more than 0.5 per cent resulting from the lye adhering to the film. The thus produced 0.5 per cent lye after reaching bath 8 would enrich there for example to 1 per cent, and then come to bath 7, where it would enrich for example to 2 per cent. This liquid would then be carried to bath 6, where some lye would be added if necessary and it will be seen that in this bath 6 it would enrich then approximately to 3 per cent. A similar addition in lye would be made in baths 5 and 4, while in baths 3 and 2 a greater addition in lye would be made and finally a still greater addition in lye would be made in bath 1, so that one would then have to work with a predetermined highest concentration, which in the example just described preferably would be 6.5 per cent.

In Fig. 3, the values on the abscissa indicate the degrees of concentrations in percentages of the ammonia in the film, and the values on the ordinate indicate the degrees of concentrations in percentages of lye in the film. Graph M shows the limit between the clear and the dull film after the coagulation. The hatched part of the chart, to the right of graph M, indicates the formation of a precipitate of $Cu(OH)_2$, when the readings of the test appear in that area and the lack of a precipitate when the readings of the concentrations appear to the left of graph M.

Graph F illustrates the concentration of the lye in the film when the process corresponds to the concentrations charted in Fig. 1, by the graph C, in which the beginning of the coagulation is represented by the point *a* while point *z* corresponds to the degrees of concentration where the film should be carried into the regeneration bath.

From the course of the graphs in Fig. 1 it will be understood that in the example given the concentration of ammonia in the film at the beginning of the coagulation would amount to 4.5 per cent and during the coagulation would drop to 2.5 per cent. This remaining 2.5 per cent will be substantially reduced in the subsequent baths to the practically insignificant concentration of 0.2 per cent. Graph C represents that at the beginning of the coagulation, the film would have a concentration of 1 per cent of caustic soda solution and that the coagulation in the example given was caused by a great and rapid increase of the lye concentration in the film resulting, in the subsequent baths immediately following the coagulation, in a concentration of 6.5 per cent. As a result of the washing then occurring, the lye, NaOH, concentration in the film drops gradually to 2 per cent.

The concentration of the lye in the treatment and the cleaning baths 2 to 9 is charted by graph B. As indicative of an increase of the dye NaOH concentration in the film, graph B appears above graph C. To indicate that the reduction of lye NaOH, by washing has started, graph B crosses graph C and thereupon remains to the end, according to the desired gradient of potential required, beneath graph C. Furthermore, the chart shows that the lye content in the film and in the treatment baths has to be considerably greater than the content of ammonia in the film.

In Fig. 3, there is charted the same process charted in Fig. 1 but from another point of view mainly from the viewpoint of the relative alkali and ammonia content in the film. Here, the coagulation process in the film is represented as starting at *a* and ending at *b*, where the subsequent treatment follows, which is completed with the last washing treatment at *z*. If a straight line were drawn from *a* to *z*, it would enter the hatched space representing the formation of a precipitate in the film, even before the termination of the coagulation. On the other hand, if the film is treated in the indirect course by the use of the high lye, NaOH, concentration, while at the same time the ammonia concentration drops gradually, in this way, which is illustrated by graph F, the hatched space is not entered until in the very last stage when the ammonia concentration in the film has been so far reduced and is so insignificant that, as aforesaid, the film cannot become soft again.

I claim:

1. The process of manufacturing foils, film stock and the like having a final thickness of substantially 0.007 to 0.12 mm. from a solution of cellulose in copperoxide ammonia characterized by spreading the solution by means of a pouring device thereupon subjecting the so spread solution to a coagulation treatment in a preliminary coagulation bath consisting of an aqueous solution of caustic alkali and ammonia of a concentration beginning with not more than 11 per cent caustic soda solution and exceeding the ammonia content in the film stock and a concentration beginning with not more than 1.2 per cent concentration of ammonia to prevent the forming of any copper hydroxide precipitate in the film stock while being coagulated, and thereupon subjecting the film stock to a succession of baths of decreasing alkali, and of decreasing ammonia content, the alkali content of each of which exceeds the ammonia content of a bath and the ammonia content of the film while passing through the baths.

2. The process of manufacturing foils, film stock and the like from a solution of cellulose in copper oxide ammonia characterized by spreading the solution by means of a pouring device, thereupon subjecting the so spread solution to a preliminary coagulation in an aqueous coagulating liquid containing caustic alkali and a lesser amount of ammonia, the caustic alkali content and the ammonia content in the liquid and in the cellulose solution being so proportioned as to preclude the precipitation of copper hydroxide from the cellulose solution, and thereupon continuing the coagulation in a series of coagulating baths of simultaneously decreasing caustic alkali and ammonia contents, the caustic alkali content in the series of baths being less than the caustic alkali content in, and exceeding the ammonia content in, the cellulose solution being coagulated at all times, the ammonia content in the coagulating liquid and in the series of baths being less than the ammonia content in the cellulose solution being coagulated at all times, to reduce gradually the alkali and ammonia content in the cellulose solution being coagulated and the caustic alkali content and the ammonia content of the series of baths being so proportioned as to preclude the precipitation of copper hydroxide from the cellulose solution.

3. The process of manufacturing foils, film stock and the like from a solution of cellulose in copper oxide ammonia characterized by spreading the solution by means of a pouring device, thereupon coagulating the so spread solution in a series of coagulating baths containing caustic alkali and ammonia and of gradually

decreasing concentration of caustic alkali and ammonia, the caustic alkali content in the series of coagulating baths exceeding the alkaline content of the cellulose solution in the first of said series of baths and being less than the caustic alkali content in the cellulose solution in the remainder of said baths and exceeding the ammonia content in the cellulose solution being coagulated at all times, the ammonia content in the series of coagulating baths being less than the ammonia content in the cellulose solution being coagulated at all times, to reduce gradually the alkali and ammonia content in the cellulose solution being coagulated during the coagulation thereof in said remainder of said series of baths and the caustic alkaline content and the ammonia content of the series of baths being so proportioned as to preclude the precipitation of copper hydroxide from the cellulose solution at all times.

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