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PROCESS OF DISSOLVING ALKALI SOLUBLE
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This invention relates to a treatment of cellu-
losic materials, more particularly to dissolving
of cellulosic materials with aqueous solutions of
caustic alkalis, and still more particularly to dis-
solving of cellulosic materials which contain
therein groups adapted to render the derivative
soluble in alkalis and which are insufficiently sub-
stituted to make them repellent toward aqueous
solutions of caustic alkalis.

The cellulosic bodies, particularly the low-sub-
stituted cellulose derivatives such as the lower
alkyl ethers and esters, unless badly degraded, re-
quire an intense solvent action in order to dissolve
them in caustic alkalis. Heretofore, this intense
action has been accomplished by chilling the cel-
lulosic bodies mixed with necessary quantities of
water and alkali, and/or by the addition of agents
to the caustic which accentuate their action,
such as urea, and certain metallic compounds. In
carrying out the solution process according to
the prior art, there have been many variations
proposed for chilling but so far as I am aware,
all of these have involved cooling of the mixture
by external means such as brine coils and like
refrigerating expedients. Thus, expensive incon-
venient equipment is required of a special nature
compared with that which is required for dissolv-
ing other substances which do not require
chilling. Further, in many instances the methods
of the prior art have proven insufficient.

This invention has as an object the treatment
of cellulosic materials with solutions of cold alkali
to obtain a more intense effect than results from
the methods of the prior art. A further object
is to provide a simplified and economical method
of dissolving or treating cellulosic materials with
cold alkali. A still further object is to provide
a method of dissolving or treating the cellulosic
materials with cold alkali which avoids the need
for complicated solution equipment used hereto-
fore in the prior art. These and other objects
will more clearly appear hereinafter.

These objects are accomplished by impregnating
the cellulosic body with a solution of caustic
alkali of greater concentration than that re-
quired in the final mixture and adding ice there-
to to provide the balance of the water and at the
same time to provide the necessary cooling effect.
Surprisingly, when this procedure is followed the
solutions which result are found to be of a con-
siderably higher quality than are obtained by
customary external cooling procedures; that is,
they contain less undissolved fibers, or in in-
stances where the cellulosic material is insoluble
it is found to be swollen to a much higher degree

than the cellulose which has been treated with
cold alkali by customary procedures. These
differences will be clearly illustrated by the ex-
amples which follow.

The invention is broadly applicable to cellulose
and low-substituted cellulose derivatives which
contain in their molecules, substituting groups
adapted to render the derivatives soluble in alka-
lis. These comprise alkali-stable esters such as
xanthate, the low-substituted cellulose ethers such
as the lower alkyl ethers, the hydroxy alkyl ethers
and hydroxy fatty acid ethers in addition to par-
tially degraded celluloses soluble in alkalis or of
cellulose which may be only swollen by alkalis.
However, it is most particularly applicable to
those cellulose derivatives which are substituted
to a low degree and which dissolve in cooled al-
kali solution, and which are insoluble or only
partly soluble in aqueous caustic alkali solutions
at room temperature. In general, the condition
and the procedures to be used in operating the
invention are governed by the principles which
have already been described in the prior art.
Thus, aqueous caustic soda solutions are found
to be better solvents than aqueous caustic potash.
Maximum solvent action is found at caustic soda
concentrations of 9 to 10% with solvent action
diminishing with either increase or decrease in
concentration. Since these requirements are well
known within the art, it is not necessary to give
the full details here.

In carrying out the invention, the cellulosic
material is first wet out with caustic alkali solu-
tion which preferably contains all of the alkali
to be used in the solution step but only a portion
of the water. It is convenient to dissolve the
alkali in about half the quantity of water to be
used in preparing the solution. Thus, if the
cellulosic material is to be dissolved in 9% sodium
hydroxide, the cellulosic material would be wet
with 18% sodium hydroxide solution. In any
case, the caustic must be dissolved in sufficient
water so that the cellulosic material can be wet
out thoroughly. This usually requires solution
equal in weight to about one and one-half times
the weight of the starting cellulosic material. The
preliminary wetting step is an important feature
of the invention since it not only simplifies the
subsequent mixing but also leads to solutions of
improved quality. The quantity of impregnating
liquor to be used will also be governed somewhat
by the quantity of ice which is to be used. Ob-
viously where little ice is needed, much impreg-
nating liquor can be used. However, it is con-
sidered advantageous to impregnate the cellulosic

material with as high a concentration of caustic as possible. Here again, the concentration will be limited because of the need of a fairly large volume of caustic to effect thorough impregnation.

5 The wetting-out with aqueous caustic is facilitated by first wetting the cellulosic material with a little water. This overcomes any surface gelatinizing effect on dry particles which might result from action of the caustic.

10 The cellulosic material which has been impregnated with the caustic alkali solution is next mixed with ice in finely divided form and in the calculated amount. Within a few moments the whole mass becomes fluid. The mass drops to a low temperature and dispersion is complete. 15 The quantity of ice to be used will depend upon the concentration and upon the temperature to which it is wished to cool the mass. This is easily calculated from the latent heat of fusion of ice, but it is preferable that no more ice than is necessary be used. Where the cellulosic material has been impregnated with a high concentration of caustic and the ice necessary to produce the desired low temperature does not provide sufficient water, then liquid water may be added 25 either to the ice or to the mixture after addition of the ice. It is preferable that the ice be finely divided since this facilitates its action. Large pieces of ice melt slowly at the temperature of solution so that their action is partly lost. After the chilling step has been effected, the mixture can be agitated thoroughly with mechanical agitation or if a less perfect solution is satisfactory, hand agitation with paddles may be sufficient.

30 The following examples illustrate my invention. Parts are by weight.

Example I

35 Sixteen hundred sixty (1660) parts of sodium methyl sulfate were dissolved in 8000 parts of sodium hydroxide. To this 80 parts of a 35% solution of "Alkanol" B were added. In this, 1000 parts of sulfite cellulose in sheet form were steeped for one hour at 28° C. The sheets were 45 pressed after steeping to a weight of 3420 parts and then placed in a close fitting sealed iron can and allowed to stand for seven days at 36° C. to effect reaction. The sheets were then thrown into a large volume of lukewarm water and disintegrated by use of a propeller-type mixer. The 50 methyl cellulose was filtered from the solution and the washing operation repeated until the fibers were caustic-free. The product was then dried.

55 (1) Six (6) parts of the dry methyl cellulose were wet out with 24 parts of water. The wet material was then mixed well with 24 parts of 30% sodium hydroxide. Forty-six (46) parts of finely crushed ice were added. This was stirred in well. The temperature of the mixture sank to 60 -6° C. A smooth, high-viscosity solution resulted which filtered excellently.

The following examples show the difference in solvent action obtained by using the ice process compared with an external refrigeration process. 65 The concentration of caustic selected for the solution is below that normally used to obtain good solutions. These concentrations were chosen, however, because they illustrate the difference in solvent action obtained by the two procedures. At higher caustic concentration the external refrigeration process can be operated to give excellent solutions. With my process, however, it is not necessary to use these high caustic concentrations. 75

(2) Six (6) parts of the dry methyl cellulose were mixed with 24 parts of water. Then 20 parts of 30% sodium hydroxide were added and the whole mixture stirred well together. Next 50 parts of finely crushed ice were incorporated 5 into the mixture and the whole stirred vigorously by hand. After two minutes the temperature of the bath had fallen to -4° C. and a smooth viscous solution had been formed. The solution upon warming to room temperature was stable 10 and filtered fairly well.

A solution of the same methyl cellulose was made, using the same procedure as in (2) except that room temperature water was added to the mixture instead of ice and the whole cooled by 15 placing in a refrigerator. A clear solution resulted which possessed a much higher fiber content than was obtained by the corresponding procedure using ice.

(3) Six (6) parts of the dry methyl cellulose were wet out well with 24 parts of water. Seven- 20 teen (17) parts of 30% sodium hydroxide were then mixed in. Next 50 parts of finely crushed ice and 3 parts of water were added and the whole agitated thoroughly by hand. The temperature dropped within a few minutes to -2.5° 25 C. and a good transparent solution which contained only a small amount of fiber resulted. On warming to room temperature the solution gelled, indicating that much material ordinarily insoluble in cold 5% sodium hydroxide solution had been dissolved under these vigorous solution conditions. 30

A solution of the same composition as (3) was prepared in the same way as (3) except that 35 room temperature water was added instead of ice. The solution was cooled to -2.5° C. by external cooling. The resulting dispersion was extremely fibrous and cloudy. It did not gel at room temperature but was of a very fibrous consistency—almost a slurry. In this instance the difference in solvent action between the ice process and the refrigeration process is extremely pronounced. 40

(4) Six (6) parts of the dry methyl cellulose were wet out with 24 parts of water and then 45 mixed with a solution of 4 parts of sodium hydroxide in 16 parts of water. Fifty (50) parts of finely crushed ice were added and the whole stirred thoroughly. A fibrous, fairly clear solution resulted which gelled on warming to room 50 temperature, indicating that much material normally insoluble in cold 4% sodium hydroxide had been dissolved. The lowest temperature reached during the process was -2° C.

A second solution of methyl cellulose was prepared in the same way as in (4) except that 55 50 parts of water at room temperature were added instead of 50 parts of finely crushed ice and the mixture cooled by placing in a refrigerator. A 60 fibrous slurry resulted which could hardly be classed as a solution. It did not gel on returning to room temperature, indicating that the solvent condition had not been sufficiently drastic to dissolve less soluble material. The product was too 65 fibrous to be useful.

Example II

One hundred sixty-two (162) grams of sulfite wood cellulose were mixed with a solution of 200 70 grams of sodium hydroxide and 1000 grams of water. Two thousand (2000) grams of finely crushed ice were added and the whole kneaded thoroughly. A dough-like mixture resulted. The temperature sank to -7° C. Three hundred 75

(300) cc. of toluene were added and stirred into the mass, followed by 760 grams of para-toluene sulfonyl chloride in 1000 grams of toluene. The mixture was allowed to stand for three days, at which time it had become acid. The mixture was washed with alcohol and then with water. The yield was 500 grams. The product contained 2.4 para-toluene sulfonyl groups. Only about one para-toluene sulfonyl group can be introduced into wood cellulose by esterification of a mass formed by cooling wood pulp mixed with dilute caustic soda solution externally. It must be concluded that the ice process gives a considerably higher degree of swelling than external refrigeration since the greater the degree of swelling of the cellulose, the greater the number of hydroxyls which are made available for reaction.

Example III

A glycol cellulose which is insoluble in caustic soda solution at room temperature but which is dissolved therein by chilling, was prepared by steeping 162 parts of sulfite wood cellulose in 20,000 parts of 18% sodium hydroxide solution for one hour at 25° C. followed by pressing to 480 parts and shredding. The alkali cellulose was placed in a baratte and 11 parts of ethylene oxide vapor were introduced. Reaction and aging were allowed to proceed for twenty hours, after which the material was then mixed with 320 parts of 20% sodium hydroxide solution followed by a mixture of 1100 parts of finely crushed ice and 500 parts of water. The mixture dissolved within a few minutes to give a perfect, viscous solution.

My procedure is particularly convenient for dissolving cellulose etherification or xanthation reaction mixtures since the preliminary wetting-out is avoided.

I believe the reason for the surprising improvement in solubility obtained by my process to be due to an osmotic action. That is, the cellulose fibers are swollen with a high concentration of an alkali (namely, caustic soda) and this, upon being mixed with water in the form of ice, is so highly swollen by the migration of water into the higher concentration of solute within the fiber that it swells to the point of solution. Thus, in addition to the solvent effect of low temperature alkali there is an additional osmotic action. This theory is confirmed by the following experiment. Six (6) parts of the methyl cellulose of Example I were wet out with 24 parts of water. The mixture was kneaded with 20 parts of 30% sodium hydroxide and the mass cooled to -6° C. Fifty (50) parts of ice water at 0° C. were then added and the whole mass stirred together thoroughly. The resulting solution was not as good as that obtained by the ice process but was better than that obtained by external refrigeration to the same temperature. While the above theory may explain my improved results, it is understood that my invention is in no way restricted to this or any theory of operation.

The cellulosic materials applicable to the invention comprise cellulose itself in any of the forms in which it occurs. This includes cellulose, degraded celluloses of every sort, and cellulose in woven or spun form or in the form of textiles. It is particularly applicable to cellulose derivatives in which the hydroxyls of the cellulose have been substituted to such a low degree that the cellulosic body is insoluble in caustic alkalis of the concentration in which it is desired to treat them at room temperature. These especially include the low-substituted ethers of cellulose such

as the lower alkyl, the hydroxy alkyl, and the hydroxy fatty acid ethers and, in addition, the alkali-stable esters such as the sulfate and xanthate. It will not include the cellulose derivatives which have become sufficiently highly substituted that they have become repellent toward solutions of caustic soda.

In carrying out the process, the ice may be added in one or several steps although it is preferred that it all be added at once in order to obtain a maximum effect. The mixture may be brought quickly back to temperature after cooling or may be held at that temperature for a prolonged period.

In order that maximum solvent action may be attained, the proportions of ice should be so adjusted that temperature falls to at least 5° C.

My invention is particularly useful in that it provides a simple method of dissolving cellulose derivatives which are soluble in cold caustic soda solutions but which are not dissolved therein at room temperature. The process also finds use with celluloses which are insoluble in alkali even with chilling, because of the high degree of swelling which results by such treatments which permit useful effects to be obtained. Thus, the highly swollen cellulose is an excellent form for many chemical reactions such as esterification by the Schotten-Baumann reaction. Textiles subjected to this treatment acquire a changed luster and a desirable permanent starched effect. The most important economic advantage, however, of the invention is that it provides a method by which these alkali-soluble, low-substituted cellulose derivatives can be dissolved without need of special equipment. The simplest form of tank provided with an agitator is all that is needed.

The above description is for purposes of illustration only, it being understood that all obvious variations and modifications coming within the spirit of my invention are to be included within the scope thereof as set forth in the appended claims.

I claim:

1. In the process of dissolving alkali-soluble cellulosic material in cold aqueous alkali, the step of cooling to dissolving temperature, the mixture of cellulosic material and caustic alkali, which comprises adding ice directly to said mixture.

2. In the process of dissolving alkali-soluble cellulose derivatives in cold aqueous caustic alkali, the step which comprises cooling a mixture of the cellulose derivative and caustic alkali of a concentration greater than that required in the final solution, by adding ice directly thereto.

3. In the process of dissolving alkali-soluble cellulose derivatives in cold aqueous caustic soda, the step which comprises cooling a mixture of the cellulose derivative and aqueous caustic soda of a concentration greater than that required in the final solution, by adding thereto ice in an amount sufficient to cool the mixture to below about 5° C., and to dilute the mixture to desired final concentration.

4. A process according to claim 3 wherein the cellulose derivative is a low-substituted methyl cellulose.

5. A process according to claim 3 wherein the cellulose derivative is a low-substituted glycol cellulose.

6. A process according to claim 3 wherein the cellulose derivative is a low-substituted cellulose glycolic acid.

7. A process for dissolving in aqueous caustic

- alkali, an alkali-soluble cellulosic material which is not water-repellent and which is insoluble in caustic alkali of the concentration of the final solution, at room temperature which comprises the steps of moistening said cellulosic material with a small amount of water, impregnating the moistened material with aqueous caustic alkali of greater concentration than that required in the final solution, and then adding ice in an amount sufficient to cool the mixture to below about 5° C. and to provide the balance of the water required, whereby dissolving of the cellulosic material is effected.
8. A process for dissolving in aqueous caustic soda, an alkali-soluble cellulosic material which is not water-repellent and which is insoluble in a caustic soda solution of about 9 to about 10% concentration, at room temperature which comprises the steps of moistening said cellulosic

material with a small amount of water, impregnating the moistened material with aqueous caustic soda of a strength substantially above 10%, and then adding ice in an amount sufficient to cool the mixture to below about 5° C. and to provide the balance of the water required, whereby dissolving of the cellulosic material is effected.

9. A process according to claim 8 wherein the cellulosic material is a low-substituted methyl cellulose.

10. A process according to claim 8 wherein the cellulosic material is a low-substituted glycol cellulose.

11. A process according to claim 8 wherein the cellulosic material is a low-substituted cellulosic glycolic acid.

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