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PRODUCTION OF WATER-SOLUBLE SALTS
OF CERTAIN CELLULOSE DERIVATIVES
OF IMPROVED PHYSICAL FORMCharles H. Rigby, Saltcoats, Scotland, assignor to
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ration of Great BritainNo Drawing. Application January 16, 1951,
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6 Claims. (Cl. 260—232)

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The present invention relates to the production of water-soluble salts of carboxymethyl cellulose of improved physical form. Sodium carboxymethyl cellulose is usually obtained in a fibrous form as a product of an etherification reaction between cellulose, sodium hydroxide and sodium chloracetate conducted in the presence of a limited amount of aqueous alcohol such that the crude product has the character of a moist fibrous solid. When it is required to prepare the sodium salt of a carboxymethyl cellulose free from the byproduct salts formed in the etherification reaction, the chemical manipulations necessary for the separation of the byproduct salts are practicable only if the fibrous form of the cellulose ether is preserved throughout these operations. The method usually adopted in the case of the water-soluble sodium salts of carboxymethyl cellulose is first to decausticise the etherification reaction mixture and then extract the byproduct salts by means of an aqueous solution of a water miscible alcohol, the initial concentration thereof being so adjusted that all the salts associated with the sodium salt of carboxymethyl cellulose dissolve, and the concentration of the alcohol being adjusted throughout the extraction so as to preserve the fibrous form of the sodium salt of carboxymethyl cellulose notwithstanding the progressive removal therefrom of the byproduct salts. This may necessitate an increase in the concentration of the alcohol as the salts are removed. Another method, which is applicable not only to water-soluble sodium salts of carboxymethyl cellulose but also to other water-soluble salts of carboxymethyl cellulose comprises conversion of the fibrous salt of carboxymethyl cellulose in the crude etherification reaction mixture into the water-insoluble free carboxymethyl cellulose while maintaining the fibrous form of the cellulose ether throughout this conversion. In this method the free carboxymethyl cellulose is thereafter washed free from salts with water and converted back into a salt of carboxymethyl cellulose by mechanical admixture with a suitable base in presence of aqueous alcohol of sufficient concentration to maintain the fibrous form of the ether throughout this conversion into a water-soluble salt thereof.

By either method the water-soluble salt of carboxymethyl cellulose is obtained in fibrous condition wet with aqueous alcohol and will retain its fibrous form after drying.

It is often required, however, to form a mixture of the dried water-soluble salt of carboxymethyl cellulose with solid powdery materials

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but it is almost impossible even after mechanical disintegration of the dry product so prepared to obtain such a mixture that will not tend to segregate because the mechanical disintegration does not destroy the fibrous structure although it reduces the length of the fibres. While it is true that the conduct of the various manipulations in such a manner as to preserve the fibrous form undamaged throughout the manipulations results in a product which can easily be dissolved in water, the fibrous product is necessarily of low bulk density.

It is an object of the present invention to provide a process for the production of water-soluble salts of carboxymethyl cellulose which will result in a product of satisfactory dissolving properties which shall be capable of easy admixture with solid powdery materials and which will also have a comparatively high bulk density, thus reducing the cost of packaging, storage and freight. The invention is especially applicable to sodium carboxymethyl cellulose from which the byproduct salts have been extracted, but it may also be applied to material that has not been purified from byproduct salts.

The remarkable discovery has been made that by subjecting the water-soluble salt of carboxymethyl cellulose wet with an aqueous solution of a water miscible alcohol to roller pressure between hard surfaces sufficient to cause it to spread under the pressure and form elements of a continuous web of at least incipiently gelatinized material the fibrous condition of the water-soluble carboxymethyl cellulose is so altered that on drying there are obtained hard brittle sheet elements which are easy to disintegrate and on disintegration yield a powdery product of relatively high bulk density capable of being easily mixed with other powdered products.

According to the present invention the method of converting into a powdery product of relatively high bulk density a water-soluble salt of carboxymethyl cellulose wet with an aqueous solution of a water miscible alcohol comprises subjecting said water-soluble salt to roller pressure between hard surfaces sufficient to cause it to spread under the pressure and form elements of a continuous web of at least incipiently gelatinized material, drying said web, and disintegrating the resulting hard brittle sheet elements to a powdery product.

The material may be in teased condition or may have been already compacted into a sheet of wet fibres by light pressure before it is subjected to the roller pressure treatment that brings about

its incipient gelation. The rolls may be cold or warm as desired. The invention is applicable not only to water-soluble sodium salts of carboxymethyl cellulose from which the saline by-products of the etherification reaction have been extracted, but also to preparations in which these salts are still present.

It is not possible to specify in numerical terms precisely what concentrations and amounts of the water miscible alcohol are the most effective for the purpose, since these may vary according to the particular salt of carboxymethyl cellulose, its degree of etherification, the content of saline impurities if present, and its viscosity characteristics, and also according to the identity of the alcohol and the characteristics of the rollers employed for the purpose. It may be necessary to adjust the concentration of the aqueous solution of the water miscible alcohol with which the water-soluble salt of carboxymethyl cellulose is wetted in order to enable it to spread under the roller pressure and form the required elements of partly gelated material, according to the characteristics of the fibrous water-soluble salt of carboxymethyl cellulose. In general there is an upper limit to the alcoholic concentration as well as a lower limit to the amount of fluid associated with the fibrous material beyond which the fibrous material will fail to form web elements of partly gelatinized material when fed to the roller apparatus, and somewhat surprisingly there may also be a lower limit to the alcoholic concentration beyond which it may be found that the roller surfaces fail to grip the fibrous material satisfactorily, depending on the manner in which it is fed. In the case of a sodium salt of carboxymethyl cellulose having a degree of substitution of 0.5 carboxymethyl groups per anhydro glucose unit and a viscosity of the order of 50 centipoises and from which the salts have been extracted and which is wet with about its own weight of aqueous ethyl alcohol, the optimum water content for this alcohol will usually lie between 45 and 50% by weight. Heavy steel roller apparatus such as is used for masticating plastic sheets may be employed, and although a multiple roller apparatus may be employed a single passage is usually sufficient to bring about the necessary partial gelatinization. Methyl alcohol and isopropyl alcohol may also be used. It can be arranged that the rollers rotate at the same or differing speeds and it will usually be found that the sheet element tends to cling to the roller that is rotating at the greater speed. During the formation of the sheet elements aqueous alcohol will usually be squeezed out of the product. With steady feeding the sheet elements will form a more or less continuous limp web of more or less opalescent appearance of low tensile strength. This may be dried off in a current of hot air and when dried is found to be brittle. The drying is quickly accomplished owing to the relatively thin form of the sheet element. The resulting dry product is disintegrated in any convenient form of mechanical disintegrator for example a multi-hammer attrition mill or a rotating opposed pin disc machine. The resulting material is a fine powder in which the fibrous structure is found to have completely disappeared. The resulting free-flowing powder mixes easily with other powdery materials and dissolves very readily in water. In this way useful compound preparations for example foodstuff preparations and detergent powders and so forth may conveniently be made. Amounts of the order of 12

kilograms pack under their own weight into about one half of the bulk that would have been required for the fibrous product from which they were made had this been dried off and disintegrated without applying the process of the invention.

The invention is illustrated in the following examples in which the parts and percentages are by weight.

Example I

90 parts of bleached sulphite woodpulp chips cut into the form of squares of 3.2 mm. side 0.7 mm. thickness and containing 8% moisture are loaded into a Werner Pfeiderer type incorporator and to this is added, after the machine has been started, 45 parts of flake caustic soda, 50 parts industrial ethyl alcohol of 7% water content and 27 parts water. The mixture is shredded and aged. Thereupon 50 parts of the same industrial ethyl alcohol are added, 34 parts of mono-chloroacetic acid are next added, and mixing is continued for a further hour with cooling. The temperature is then raised to 60° C. at which temperature the mixture is maintained for 45 minutes to complete the reaction and to effect some slight reduction in viscosity of the product. The reaction mixture is cooled to 30° C. and brought into a slurry with 17 times its weight of aqueous industrial ethyl alcohol of a concentration sufficient to ensure the dissolution of the salts present without destroying the fibrous character of the product, and a quantity of nitric acid sufficient to neutralise its free alkalinity is added. The product is then centrifuged and after the bulk of the liquor has been removed it is sprayed with 8 times its weight of aqueous ethyl alcohol of 45% water content by weight and again centrifuged. The product is spun until the aqueous ethyl alcohol ceases to flow away from it. The resulting mass of fibrous material containing 52.5% of its weight of aqueous ethyl alcohol is teased out and fed into the nip of a 230 mm. diameter pair of unheated steel rollers rotating one at 20 and the other at 30 revolutions per minute. The rollers are set so as to touch and it is found that the product enters the nip satisfactorily and adheres to the faster of the rollers thereafter in the form of a more or less continuous sheet of material showing visual evidence by its opalescent appearance that some gelatinization has taken place. The product is then dried off in a current of hot air and the resulting brittle sheet is broken up and mechanically disintegrated in a multi-hammer mill through a grid containing circular perforations each of 0.40 mm. diameter as a result of which the fibrous form entirely disappears and the product becomes a fine powder of which 85% passes through a 100 British Standard Specification screen. The viscosity of an aqueous solution containing 1% by weight of the material so produced is of the order of 58 centistokes and the degree of substitution is 0.49. The product mixes very easily with pulverised sodium sulphate or flour without tending to segregate on subsequent shaking and dissolves very easily in water. Its bulk density is 0.82 gm. per cc. as compared with 0.4 gm. per cc. for material prepared and disintegrated in the same manner except for the omission of the rolling treatment, and its subjection to a longer period of disintegration rendered necessary by the unmodified fibrous nature of the dried product.

Example II

90 parts of sulphite woodpulp chips cut into the form of squares of $\frac{1}{8}$ inch side and containing 8% moisture is loaded into a Werner Pfleiderer type incorporator and to this is added, after the machine has been started, 45 parts of flake caustic soda, 50 parts industrial ethyl alcohol of 7% water content and 37 parts water. The mixture is shredded and aged under conditions favouring substantial reduction in viscosity. Thereupon 50 parts of the same industrial ethyl alcohol are added, 38 parts of mono-chloracetic acid are next added and mixing is continued for a further hour with cooling. The temperature is then raised to 60° C. at which temperature the mixture is maintained for two hours to complete the reaction and effect some further reduction in the viscosity of the product. The reaction product is cooled to 30–35° C. over a period of about half an hour and 28 parts sodium bicarbonate are incorporated into it in order to convert the excess sodium hydroxide into sodium carbonate.

The moist product at this stage has a total volatile matter content of 37.5% which consists of approximately 20% alcohol and 17.5% water, and is in the form of a loose fibrous mass. It is fed into the nip of a pair of unheated steel rollers (of 230 mm. diameter) rotating one at 20 and the other at 30 revolutions per minute. The rollers are set so as to touch and it is found that the product enters the nip satisfactorily and adheres to the faster of the two rollers thereafter in the form of a more or less continuous opaque sheet showing visible evidence of incipient gelatinization of the sodium carboxymethyl cellulose contained therein.

The product is then dried off in a current of hot air and the resultant brittle sheet is broken up and mechanically disintegrated in a multi-hammer mill through a grid containing circular perforations each of 0.4 mm. diameter as a result of which the fibrous form entirely disappears and the product becomes a fine powder of which 77% passes through a 100 British Standard Specification screen. The bulk density of the powdered product is 0.87 gm. per cc. as compared with 0.56 gm. per cc. for material prepared, dried and disintegrated in the same manner except for the omission of the rolling treatment. Moreover the fibrous structure can be clearly seen in the unrolled disintegrated material. The degree of substitution of the powdered material so obtained is 0.50 and a solution containing 4% by weight of it has a viscosity of the order of 46 centistokes.

Example III

90 parts of bleached sulphite woodpulp chips cut into the form of squares of 3.2 mm. side and 0.7 mm. thickness and containing 8% moisture are loaded into a Werner Pfleiderer type incorporator and to this is added, after the machine has been started, 33 parts of flaked caustic soda, 50 parts of industrial ethyl alcohol of 7% water content and 27 parts water. The mixture is shredded and aged. Thereupon 50 parts of the same industrial ethyl alcohol are added, 85 parts of the sodium salt of monochloracetic acid are next added and mixing is continued for a further hour with cooling. The temperature is then raised to 60° C. at which temperature the mixture is maintained for 45 minutes to complete the reaction. The reaction mixture is cooled to 30° C. and brought into slurry with 17 times its weight of aqueous ethyl alcohol of 35% water

content by weight and a quantity of nitric acid sufficient to neutralise its alkalinity is added. The product is then centrifuged and after the bulk of the liquor has been removed, it is sprayed with 8 times its weight of aqueous industrial ethyl alcohol of the same concentration. The product is spun until the aqueous ethyl alcohol ceases to flow away from it. The resulting mass of fibrous material at this stage contains 27% water and 26.5% of alcohol. It is teased out and fed into the nip of a pair 230 mm. diameter steel unheated rollers rotating one at 20 and the other at 30 revolutions per minute. The rollers are set so as to touch and the product adheres to the faster roller in the form of a more or less continuous opalescent sheet. The product is dried in a current of hot air and the resulting brittle sheet is broken up and mechanically disintegrated in a multi-hammer mill through a grid containing circular perforations each of .4 mm. diameter as a result of which a free-flowing fine powder is obtained of which 88% passes through a 100 British Standard Specification screen. The powdered material mixes very easily with powdered sodium sulphate or flour without tending to segregate. Its bulk density is 0.74 gm. per cc. as compared with 0.34 gm. per cc. for material prepared and disintegrated in the same manner except for the omission of the rolling treatment.

The degree of substitution is 0.7 and the viscosity of a 1% aqueous solution is of the order of 38 centistokes.

Example IV

90 parts of bleached sulphite woodpulp chips cut into the form of squares of 3.2 mm. side 0.7 mm. thickness and containing 8% moisture are loaded into a Werner Pfleiderer type incorporator and to this is added, after the machine has been started, 45 parts of flake caustic soda, 50 parts industrial ethyl alcohol of 7% water content and 27 parts water. The mixture is shredded and aged. Thereupon 50 parts of the same industrial ethyl alcohol are added, 34 parts of mono-chloracetic acid are next added, and mixing is continued for a further hour with cooling. The temperature is then raised to 60° C. at which temperature the mixture is maintained for 45 minutes to complete the reaction and to effect some slight reduction in viscosity of the product.

The reaction mixture is cooled to 30° C. and brought into a slurry with 17 times its weight of aqueous isopropyl alcohol of 47.5% water content. A quantity of nitric acid sufficient to neutralise its free alkalinity is then added and the product is centrifuged. After the bulk of the liquor has been removed it is sprayed with 8 times its weight of the same aqueous isopropyl alcohol and again centrifuged. The product is spun until the aqueous isopropyl alcohol ceases to flow away from it. The resulting fibrous mass is teased out and fed into the nip of a pair of 230 mm. diameter steel unheated rolls rotating one at 20 and the other at 30 revolutions per minute. The rollers are set so as to touch and the product adheres to the faster roller in the form of a more or less continuous opalescent sheet. The product is dried in a current of hot air and the resulting brittle sheet is broken up and mechanically disintegrated in a multi-hammer mill through a grid containing circular perforations each of 0.4 mm. diameter as a result of which a free flowing fine powder is obtained of which 94% passes through a 100 British Standard Specification screen. The product mixes very

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easily with powdered sodium sulphate or flour without tending to segregate. Its bulk density is 0.74 gm. per cc. as compared with 0.4 gm. per cc. for material prepared and disintegrated in the same manner except for the omission of the rolling treatment.

What I claim is:

1. A method of converting a fibrous water soluble sodium salt of carboxymethyl cellulose into a powdered form of relatively high bulk density in comparison with the bulk density realized by comminuting said carboxymethyl cellulose in fibrous form which comprises subjecting a fibrous water soluble sodium salt of carboxymethyl cellulose wet with an aqueous solution of a water miscible alcohol in which said carboxymethyl cellulose is insoluble so that the fibrous structure of said carboxymethyl cellulose is retained in said solution, which alcohol boils at a boiling point below the boiling point of water, to roller pressure between hard surfaces to cause said carboxymethyl cellulose to spread under the pressure and form elements of a continuous web of at least incipiently gelatinized material, drying said web and comminuting the resulting hard brittle sheet elements to a powdery product.

2. A method as recited in claim 1 in which said

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water miscible alcohol is selected from the group consisting of methyl, ethyl and isopropyl alcohols.

3. A method as claimed in claim 1 wherein the water soluble salt of carboxymethyl cellulose is sodium carboxymethyl cellulose free from by-product salts.

4. A method as claimed in claim 1 wherein the water soluble salt of carboxymethyl cellulose is in teased condition prior to being subjected to said pressure treatment.

5. A method as claimed in claim 1 wherein the water soluble salt of carboxymethyl cellulose is compacted by light pressure into a sheet of wet fibers prior to being subjected to said pressure treatment.

6. A method as claimed in claim 1 wherein the water miscible alcohol is ethyl alcohol.

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