

PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION.

Improvements in or relating to the Manufacture of Benzyl Cellulose.

We, IMPERIAL CHEMICAL INDUSTRIES, LIMITED, a Company registered under the laws of Great Britain, of Broadway Buildings, Westminster, London, S.W. 1, and DAVID TRAILL, a subject of the King of Great Britain and Ireland, of 17, Ardrossan Road, Saltcoats, Ayrshire, Scotland, do hereby declare the nature of this invention to be as follows:—

10 This invention relates to benzyl celluloses.

It has for its object to provide improved or modified benzyl celluloses, or improved or modified processes for producing and utilizing benzyl celluloses.

15 The invention consists in an improved method for the manufacture of benzyl celluloses, in which the cellulose is first intimately mixed with a mercerising caustic soda solution and this preliminary treatment is followed by a maturing treatment at a temperature between 10° C. and 35° C.

20 The invention also consists in a process according to the preceding paragraph, according to which after maturing for periods which may be varied, the cellulose is treated with powdered caustic soda and benzyl chloride to give the required degree of benzylation, preferably a high degree of benzylation.

25 The invention also consists in the application of the benzyl cellulose when prepared according to either of the preceding two paragraphs, in the preparation of lacquers, including brushing and spraying lacquers, varnishes, enamels, wood finishes, leather cloth finishes, cinematograph, photograph and other films, splinterless glass, artificial silk and the like.

30 The invention also consists in the colouration of the benzyl cellulose referred to in the preceding paragraph by fast and other dyestuff processes.

35 The invention also consists in processes for the manufacture of benzyl cellulose substantially as hereinafter described.

40 The invention further consists in application of benzyl cellulose substantially as hereinafter described.

45 The invention further consists in products when prepared by processes substan-

tially as hereinafter described, or by the obvious chemical equivalents of those processes. 55

The following examples illustrate how the invention may be carried into effect, all parts being parts by weight:—

EXAMPLE 1.

60 100 parts by weight of cellulose are mercerised for any suitable time up to 24 hours, but preferably for one hour, with a caustic soda solution, 15% to 50%, and are then pressed to 200—400 parts by weight. After being finely shredded in a Werner-Pfleiderer or some such suitable machine, the soda cellulose is matured for two days at a temperature above room temperature but below 35° C. 70 50 to 100 parts of finely powdered caustic soda are added and intimately mixed. This mixing may take place in a reaction kettle with very efficient stirring gear, or may be first carried out in a Werner-Pfleiderer machine. 75 150—300 parts of benzyl chloride are added, and the whole is thoroughly mixed. The mixture is heated in a vessel provided with a reflux condenser with stirring, on a water bath, 80 or alternatively the reaction may be carried out in a steam jacketed kettle, the temperature of heating preferably being about 100° C., and the heating preferably being continued for about 85 8—10 hours. Different temperatures may be employed with a variation of time. A further 150—300 parts of benzyl chloride is added, and the mixture is heated for another 8 to 10 hours, after which time 100—200 parts of benzyl chloride are added, and the heating is continued for 10—20 hours. The reaction product is a yellow gummy mass. It is malaxated with alcohol and, after thorough mixing for 10—30 minutes, filtered. 95

The filtrates may be collected and later fractionated, when the excess of benzyl chloride and reaction products such as benzyl alcohol and benzyl ether are isolated. 100

After several such alcohol treatments, during which the product becomes less and less gummy and is ultimately obtained in a granular form, the product 105

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is treated with ether and then filtered. The compound is now freed from sodium chloride by washing with water. It is finally washed with alcohol, dried, and, if desired, powdered. The benzyl cellulose is thus obtained in the form of a fine white powder.

The viscosities of 10% solutions of the benzyl cellulose produced as described in this Example, when it is dissolved in a mixture of benzene and alcohol in the proportion of 90% by volume of the former to 10% by volume of the latter generally vary between 1 and 10 c.g.s. units, according to the concentration of caustic soda, time and temperature of maturing of the soda cellulose, time of heating of the reaction mass and so on.

EXAMPLE 2.

100 parts of cellulose are mercerised with caustic soda solutions (15% to 50%) and treated in a manner similar to that described in Example 1. After maturing at 20° C. to 30° C. for six days, the soda cellulose is treated with caustic soda and benzyl chloride as described in Example 1. The product may be purified in the same way.

Viscosities of 10% solutions of the products in a mixture of 90% benzene 10% alcohol are generally 0.02—1 c.g.s. units, but may be either higher or lower.

As illustrated by the above examples, by varying the time and conditions of maturing within the limits specified the soda cellulose, benzyl cellulose of practically any desired viscosity may be obtained.

GENERAL.

Water soluble and alkali soluble benzyl ethers of cellulose have been referred to previously, and admitted to be of a low degree of etherification. In other cases, a high degree of etherification has been claimed.

According to the present invention, etherification takes place without isolation of the intermediate products, and it is essential that the alkali cellulose produced shall be matured. By maturing for different times and at different temperatures within the limits specified, the process is variable in such a manner as to give products of differing viscosity and solubility. It is thus possible to produce benzyl cellulose suited for different technical applications, amongst which may be mentioned enamels, wood finishes, brushing and spraying lacquers, protective coatings, films, artificial silk, gramophone records, compound glass, insulators, leather-cloth, celluloid or moulding powders.

A typical analysis of a benzyl cellulose produced by our method is

C=69.8%; H=6.40%
 $C_6H_5O_5$ ($CH_2C_6H_5$)₅ requires
 C=70.17%; H=6.58%

This method of manufacture is specially suitable for a process which starts with wood pulp as its raw material, but any other form of cellulose or cellulose hydrate, such as cotton cellulose, paper, artificial silk waste, or the like may be employed.

It is preferred that an intimate mixture of cellulose and caustic soda be effected by mercerising the cellulose with the caustic soda of suitable concentration, and then pressing it to from 2½ to 4 times the original weight, after which it is comminuted in a Werner-Pfleiderer mixer or the like. After this the soda cellulose is matured above room temperatures but less than 35° C., and this maturing is followed by a thorough mixing with caustic soda, for example, in a reaction kettle. The intimate mixture obtained by the two stages of mixing, employing only a small quantity of water, appears to result in a high degree of benzylation, while the varying of the time of maturing of the soda cellulose, before treating it with the benzylating agent, varies the viscosity and the solubility of the resulting benzyl cellulose.

The cellulose is mercerised with caustic soda solution, 15% to 50%, for any time up to 24 hours, but preferably for one hour, and the mercerised cellulose is then pressed to from about 2½ to 4 times the original weight of the cellulose. The soda cellulose thus obtained is finely shredded by means of a Werner-Pfleiderer or such machine, and the shredded material is stored for varying times at 25° C., but may be kept for a longer or shorter time at a lower or higher temperature between the stated limits if desired. The time of maturing is varied according to the viscosity required, and according to the temperature at which the soda cellulose has been maintained.

The properties of the benzyl cellulose may be still further varied by the addition of oxidising or of reducing agents to the maturing soda cellulose.

When maturing is complete, the finely shredded soda cellulose is mixed with finely powdered caustic soda; to this mixture benzyl chloride is added. The mixture is stirred and heated, preferably at about 100° C. for varying times. The benzyl chloride is preferably added in several quantities at intervals during the heating, but the full quantity may be added in one addition if desired. Diluents, such as benzene, may be employed.

The reaction product is generally a

gummy, yellow paste, containing benzyl cellulose, benzyl chloride, benzyl alcohol, benzyl ether, sodium chloride, condensation products and possibly degradation products, and is difficult to work. By the present process the cellulose ether may be obtained by malaxating the reaction product first with industrial spirits and then filtering or centrifuging. The sodium chloride is removed by washing the residue with hot water until the product is free from chloride. It is then again malaxated with industrial spirits, centrifuged and dried.

The reaction product may sometimes be in a hard gummy condition in which case it may be powdered and treated several times with hot water before receiving the treatment outlined above.

The product is soluble in benzene-alcohol, toluene-alcohol, acetone-benzene, chloro-derivatives of ethane and ethylene-alcohol mixtures, cyclohexanol, benzyl alcohol, furfural and the like. Various plasticisers, for example, triphenyl phosphate, tricresyl phosphate, dibutyl plthalate or camphor may be employed in the working up of the cellulose ether. The non-inflammability and almost complete impermeability to water recommend the product thus obtained for many technical applications, whose requirements may be satisfied, as regards viscosity, by the method outlined above.

The invention is not limited to the use of the solvents described for the purification of benzyl cellulose, and the purification may be effected for example by other organic solvents than those mentioned or by a combination of organic solvents which dissolve the by-products formed, and do not dissolve or gelatinise the benzyl cellulose.

Dated this 2nd day of October, 1928.
MARKS & CLERK.

COMPLETE SPECIFICATION.

Improvements in or relating to the Manufacture of Benzyl Cellulose.

We, IMPERIAL CHEMICAL INDUSTRIES, LIMITED, a Company registered under the laws of Great Britain, of Imperial Chemical House, Millbank, London, S.W. 1, formerly of Broadway Buildings, Westminster, London, S.W. 1, and DAVID TRAILL, a subject of the King of Great Britain and Ireland, of 17, Ardrossan Road, Saltcoats, Ayrshire, Scotland, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to benzyl celluloses.

It has for its object to provide improved or modified benzyl celluloses, or improved or modified processes for producing and utilizing benzyl celluloses.

The invention consists in a process for the manufacture of benzyl cellulose insoluble in aqueous alkali according to which the cellulose is first mixed with a mercerising caustic soda solution of about 18% to 20% concentration, and this preliminary treatment is followed by the pressing of the product until it weighs from $2\frac{1}{2}$ to 4 times the weight of cellulose raw material, after which it is matured at a temperature between 22 and 35° C. and then intimately mixed with from 50 to 100 parts of solid caustic soda for each 100 parts by weight of cellulose raw material used, the product then being benzylated.

The invention also consists in the application of benzyl cellulose, when prepared according to the preceding paragraph, in the preparation of lacquers, including brushing and spraying lacquers, varnishes, enamels, wood finishes, leather cloth finishes, cinematograph, photograph and other films, splinterless glass, artificial silk or moulding powders.

The invention also consists in the colouration of benzyl cellulose when prepared by the processes indicated above, for instance, by fast or other dyestuffs.

The invention also consists in processes for the manufacture of benzyl cellulose derivatives substantially as hereinafter described.

The invention further consists in the applications substantially as described of benzyl cellulose derivatives when prepared substantially as herein described.

The invention further consists in products when prepared by processes substantially as herein described, or by the obvious chemical equivalents of those processes.

The following examples illustrate how the invention may be carried into effect, all parts being parts by weight:—

EXAMPLE 1.
100 parts by weight of air dried cellulose

loses are mercerised for any suitable time up to 24 hours, but preferably for one hour, with a caustic soda solution of a concentration of about 18% to 20%, and are then pressed to 250—400 parts by weight. After being finely shredded in a Werner-Pfleiderer or some such suitable machine, the soda cellulose is matured for two days at a temperature between 22 and 35° C. A further 50 to 100 parts of solid caustic soda are added and intimately mixed. This mixing may take place in a reaction kettle with very efficient stirring gear, or may be first carried out in a Werner-Pfleiderer machine. 150—300 parts of benzyl chloride are added, and the whole is thoroughly mixed. The mixture is heated in a vessel provided with a reflux condenser with stirring on a water bath, or alternatively the reaction may be carried out in a steam jacketed kettle, the temperature of heating preferably being about 100° C., and the heating preferably being continued for about 8—10 hours. A further 150—300 parts of benzyl chloride are added, and the mixture is heated for another 8 to 10 hours, after which time 100—200 parts of benzyl chloride are added, and the heating is continued for 10—20 hours. The reaction product is a yellow, gummy mass. It is malaxated with alcohol and, after thorough mixing for 10—30 minutes, filtered. Different temperatures for carrying out the benzylation may be employed with a variation of time.

The filtrates may be collected and later fractionated, when the excess of benzyl chloride and reaction products such as benzyl alcohol and benzyl ether are isolated.

After several such alcohol treatments, during which the product becomes less and less gummy and is ultimately obtained in a granular form, the product is treated with ether and then filtered. The compound is now freed from sodium chloride by washing with water. It is finally washed with alcohol, dried, and, if desired, powdered. The benzyl cellulose is thus obtained in the form of a fine white or whitish powder.

The viscosities of 10% solutions of the benzyl cellulose produced as described in this Example, when it is dissolved in a mixture of benzene and alcohol in the proportion of 90% by volume of the former to 10% by volume of the latter generally vary between 1 and 10 c.g.s. units, according to the pressing, the amount of added caustic soda, time and temperature of maturing of the soda cellulose within the prescribed limits of temperature, time of heating of the reaction mass and so on.

EXAMPLE 2.

100 parts of air-dried cellulose are mercerised with caustic soda solutions of a concentration of about 18% to 20%, and treated in a manner similar to that described in Example 1.

After maturing at 22° C. to 30° C. for six days, the soda cellulose is treated with solid caustic soda and benzyl chloride as described in Example 1. The product may be purified in the same way.

Viscosities of 10% solutions of the products in a mixture of 90% benzene 10% alcohol are generally 0.02—1 c.g.s. units, but may be either higher or lower.

EXAMPLE 3.

100 parts of air-dried cellulose are mercerised with a caustic soda solution of a concentration of about 18% to 20% for 1—2 hours, and pressed until the product weighs approximately 2½ times the weight of cellulose raw material. After shredding in a Werner-Pfleiderer incorporator, fitted with dentated sigma blades, for 3—4 hours, the soda cellulose is placed in a maturing room at 22—30° C., preferably 25° C., for 60—90 hours. The soda cellulose is then placed in a jacketed reaction kettle and intimately mixed with 50 parts of powdered caustic soda and 150 parts of benzyl chloride are added. The soda cellulose and powdered caustic soda may undergo a preliminary mixing in a Werner-Pfleiderer incorporator before placing in the reaction kettle. The mixture is heated for 8 hours, stirring continuously and keeping the temperature at 95—110° C. A further addition of 150 parts of benzyl chloride is made and the mixture heated for 16 hours. The reaction mass is removed from the kettle while still warm, and is then purified by intensive mixing with industrial spirit in any efficient mixing machine. The alcoholic extraction liquors are run off and the residue is centrifuged, washed free from chloride with water and dried. The dried product is white or whitish and granular, and dissolves in the solvents referred to below. The viscosity of a 10% solution of a benzyl cellulose produced in this way is 4—8 c.g.s. (in a toluene—spirits mixture 80:20 by volume) but benzyl celluloses of higher viscosity, 20—200 c.g.s. units per 10% solution, may be prepared by varying the conditions of maturing within the prescribed limits of temperature. The product just referred to is specially suitable for thermo-plastic work.

GENERAL.

According to the present invention, etherification takes place without isolation of the intermediate products, and it

is essential that the alkali cellulose produced shall be matured. By maturing for different times and at different temperatures within the prescribed limits of temperature the process is variable in such a manner as to give products of differing viscosity and solubility in organic solvents. It is thus possible to produce benzyl cellulose suited for different technical applications, amongst which may be mentioned enamels, wood finishes, brushing and spraying lacquers, protective coatings, films, artificial silks, gramophone records, compound glass, insulators, leather cloth, celluloid or moulding powders. A typical analysis of a benzyl cellulose produced by our method is

C=69.8%; H=6.40%
 $C_6H_8O_5 (CH_2C_6H_5)_2$ requires
 C=70.17%; H=6.58%

A typical analysis of a soda cellulose pressed to three times the weight of cellulose raw material prepared as described above after pressing and comminuting but before maturing, is as follows:—

| | |
|-----------------------|--------|
| Sodium hydroxide | 11.96% |
| Sodium carbonate | 1.16% |
| Cellulose | 30.07% |
| Water (by difference) | 56.81% |
| | 100.00 |

The corresponding ratio water to the weight of cellulose raw material = $\frac{56.81 \times 3}{100} = 1.70$.

The method of manufacture is specially suitable for a process which starts with wood pulp as its raw material, but any other form of cellulose or cellulose hydrate, such as cotton cellulose, paper, artificial silk waste, or the like, may be employed.

An intimate mixture of cellulose and caustic soda is prepared by mercerising the cellulose with a caustic soda solution of a concentration of about 18% to 20% and after pressing it to from $2\frac{1}{2}$ to 4 times the original weight of cellulose raw material, it is comminuted in a Werner-Pfleiderer mixer or the like. After this, the soda cellulose is matured at a temperature between 22 and 35° C. and this maturing is followed by a thorough mixing with from 50 to 100 parts of solid caustic soda for each 100 parts by weight of cellulose raw material used, for example, in a reaction kettle. The intimate mixture obtained by the two stages of mixing appears to result in a high degree of benzylation, while the varying of the time of maturing of the soda cellulose within the prescribed limits of temperature, before treating it with the

benzylating agent, varies the viscosity and the solubility of the resulting benzyl cellulose in organic solvents.

The cellulose is mercerised with a caustic soda solution of a concentration of about 18% to 20% for any time up to 24 hours, but preferably for one hour, and the mercerised cellulose is then pressed to from about $2\frac{1}{2}$ to 4 times the original weight of cellulose raw material. The soda cellulose thus obtained is finely shredded, by means of a Werner-Pfleiderer or such machine, and the shredded material is stored for varying times at 25° C., but may be kept for a longer or shorter time at a lower or higher temperature between the stated limits if desired. The time of maturing is varied according to the viscosity required, and according to the temperature at which the soda cellulose has been maintained.

The properties of the benzyl cellulose may be still further varied by the addition of oxidising or of reducing agents to the maturing soda cellulose.

When maturing is complete, the finely shredded soda cellulose is mixed with 50—100 parts finely powdered caustic soda for each 100 parts by weight of cellulose raw material used; to this mixture benzyl chloride is added. The mixture is stirred and heated, preferably about 100° C. for varying times. The benzyl chloride is preferably added in several quantities at intervals during the heating, but the full quantity may be added in one addition, if desired. Diluents, such as benzene, may be employed.

The reaction product is generally a gummy, yellow paste, containing benzyl cellulose, benzyl chloride, benzol alcohol, benzyl ether, sodium chloride, condensation products and possibly degradation products, and is difficult to work. By the present process the cellulose ether may be obtained by malaxating the reaction product first with industrial spirits and then filtering or centrifuging. The sodium chloride is removed by washing the residue with hot water until the product is free from chloride. It is then again malaxated with industrial spirits, centrifuged and dried.

The reaction product may sometimes be in a hard gummy condition, in which case it may be powdered, and treated several times with hot water before receiving the treatment outlined above.

The product is soluble in benzene-alcohol, in toluene-alcohol, in acetone-benzene, in mixtures of alcohol with chloro-derivatives of ethane and of ethylene, in cyclohexanol, in benzyl alcohol and in

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furfural. Various plasticisers, for example, triphenyl phosphate, tricresyl phosphate, dibutyl phthalate, para-toluene sulphanilide, benzyl benzoate, 5 benzyl abietate (Boake, Roberts & Co., London), zinc butyl phthalate, xylene sulphoamide, phenyl urethane, diethyl diphenyl urea, amyl tartrate, monochlorhydrin, triacetin, resorcinol diacetate, 10 glyceroltribenzoate, dicresyl ether of glycerol, tolyl carbonate, the ethyl ester of phenyl oxamic acid, or camphor may be employed in the working up of the cellulose ether. The non-inflammability 15 and almost complete impermeability to water recommend the product thus obtained for many technical applications, whose requirements may be satisfied, as regards viscosity, by the method outlined 20 above.

The invention is not limited to the use of the solvents described for the purification of benzyl cellulose and the purification may be effected for example by other 25 organic solvents than those mentioned or by a combination of organic solvents which dissolve the by-products formed and do not dissolve or gelatinise the benzyl cellulose.

30 Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that we make no claim to anything described or claimed 35 in Specification No. 177,809 but what we claim is:—

1. A process for the manufacture of benzyl cellulose insoluble in aqueous alkali according to which the cellulose

is first mixed with a mercerising caustic 40 soda solution of about 18% to 20% concentration, and this preliminary treatment is followed by the pressing of the product until it weighs from $2\frac{1}{2}$ to 4 times 45 the weight of cellulose raw material, after which it is matured at a temperature between 22 and 35° C., and then intimately mixed with from 50 to 100 parts of solid caustic soda for each 100 50 parts by weight of cellulose raw material used, the product then being benzylated.

2. The process which consists in the application of benzyl cellulose when prepared according to Claim 1, in the preparation of lacquers including brush- 55 ing and spraying lacquers, varnishes, enamels, wood finishes, leather cloth finishes, cinematograph, photograph and other films, splinterless glass, artificial 60 silk or moulding powders.

3. The process which consists in the colouration of benzyl cellulose when prepared by the process of Claim 1, by fast or other dyestuffs.

4. Processes for the manufacture of benzyl cellulose derivatives substantially 65 as described.

5. Processes which consist in the applications substantially as described of benzyl cellulose derivatives when prepared 70 by the processes of Claims 1, 3 and 4.

6. Products when prepared by the processes of any of the above claims, or by the obvious chemical equivalents of those 75 processes.

Dated this 19th day of June, 1929.
MARKS & CLERK.