

PATENT SPECIFICATION

Application Date : June 11, 1930. No. 17,924 / 30.

356,308

Complete Left : March 9, 1931.

Complete Accepted : Sept. 10, 1931.

PROVISIONAL SPECIFICATION.



Improvements in or relating to the Manufacture of Cellulose Ethers.

We, ALFRED STOVELL LEVESLEY, Chemist, of 21, Caledonia Road, Saltcoats, Ayrshire, FREDERICK CHARLES RANDALL, Chemist, of 76, Eglinton Road, Ardrossan, both subjects of the King of Great Britain, and IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W. 1, a Company registered under the laws of Great Britain, do hereby declare the nature of this invention to be as follows:—

In co-pending applications Nos. 5659/29 (Serial No. 333,902) and 12,035/30 kieriing processes are described for the production of cellulose ethers of substantially uniform low viscosity. These processes consist in heating the cellulose ether with an acid or with alkyl- or aralkyl-halides under pressure. On account of the thermoplastic nature of the cellulose ethers the product obtained as a result of such treatment may consist, when hot, of a soft spongy mass which on cooling sets to a solid cake. This cake is in more or less tough condition according to the temperature and duration of the kieriing treatment and the softening point of the cellulose ether. The grinding process, to which the product is subsequently submitted, therefore presents certain difficulties, and this is particularly the case with the product of the processes described in application No. 5659/29 (Serial No. 333,902), owing to the plasticising action of the alcohol produced by hydrolysis of the alkyl- or aralkyl-halide used in the kieriing process.

We have now found that these difficulties may be avoided by performing the kieriing operation in the presence of a sufficient quantity of a water-soluble salt, or of a mixture of such salts. We prefer to use for this purpose salts which have approximately the same solubility at raised as at ordinary temperatures (e.g. sodium chloride or potassium chloride) or salts which are more soluble in cold water than in hot (e.g. sodium citrate). The quantity of salt used should be sufficient to give a highly concentrated or even saturated solution at the highest temperature reached during the kieriing process. The products

[Price 1s.]

obtained according to our invention are easily ground and are indeed in many cases in such a condition as to require no grinding.

Any excess of solid salt may be recovered after the kieriing treatment, and the concentration of the kieriing liquor may be adjusted for further use by the addition of fresh kieriing agent.

Our invention is applicable not only to the processes of the co-pending applications already mentioned but also to other processes in which cellulose ethers are submitted to a kieriing treatment.

Our invention is illustrated but not limited by the following examples the parts and percentages of which are by weight.

EXAMPLE 1.

100 parts of benzyl cellulose which has a viscosity of approximately 100 c.g.s. units in 10% solution in toluene spirits mixtures (80 : 20) are kieried with 700 parts of 0.75% oxalic acid solution and 300 parts of sodium citrate for 3/4 hour. The kieried mass is a discrete powder. It is washed free from acids and salts, and dried. The viscosity in 10% solution in toluene spirits (80 : 20) is 5 c.g.s. units.

EXAMPLE 2.

50 parts of ethyl cellulose with a viscosity of 250 c.g.s. units when measured in 10% solution in benzene, are kieried in a closed vessel with 575 parts of a solution containing approximately 0.95% of its weight of hydrochloric acid and 250 parts of commercial sodium chloride for a period of 30 mins. at a pressure of 25 lb. per sq. in. The resulting product in the kier is still in a loose non-caked condition, which can be easily ground in a mechanical mortar and washed free from impurities. The viscosity after purification measures 5 c.g.s. units in a 10% solution in benzene.

EXAMPLE 3.

100 parts of a partially purified benzyl cellulose reaction mass, which contains about 5—15% of benzyl chloride, and a portion of which when purified gives a viscosity of 25 c.g.s. units in a toluene spirit mixture (80 : 20) are heated with 1000 parts of water and 500 parts of com-

mercial sodium chloride, for 3/4 hour at 25 lb. per sq. in. pressure.

The kiered product is a loosely cohering friable mass, which is easily ground in a mechanical mortar. When washed free from salts and dried, the product gives clear solutions with a viscosity such that

it is eminently suitable for the preparation of lacquers and enamels.

Dated the 10th day of June, 1930.

E. C. G. CLARKE,
Imperial Chemical House,
Millbank, London, S.W. 1,
Solicitor for the Applicants.

COMPLETE SPECIFICATION.

Improvements in or relating to the Manufacture of Cellulose Ethers.

- 10 We, ALFRED STOYELL LEVESLEY, Chemist, of 21, Caledonia Road, Saltcoats, Ayrshire, FREDERICK CHARLES RANDALL, Chemist, of 76, Eglinton Road, Ardrossan, both subjects of the King of Great Britain, and IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W. 1, a Company registered under the laws of Great Britain, 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:—
- 25 In co-pending applications Nos. 5659/29 (Serial No. 333,902) and 12,035/30 kiering processes are described for the production of cellulose ethers of substantially uniform low viscosity. These processes consist in heating the cellulose ether with an acid or with alkyl- or aralkyl-halides under pressure. On account of the thermoplastic nature of the cellulose ethers at elevated temperatures the product obtained as a result of such treatment may consist, when hot, of a soft spongy mass which on cooling sets to a solid cake. This cake is in more or less tough condition according to the temperature and duration of the kiering treatment and the softening point of the cellulose ether. The grinding process, to which the product is subsequently submitted, therefore presents certain difficulties. This is particularly the case with the product of the processes described in application No. 5659/29 (Serial No. 333,902), owing to the plasticising action of the alcohol produced by hydrolysis of the alkyl- or aralkyl-halide used in the kiering process.
- 30 We have now found that these difficulties may be avoided by performing the kiering operation in the presence of a sufficient quantity of a water-soluble non-acid salt, or of a mixture of such salts. We prefer to use for this purpose salts which have approximately the same solubility both at high and at ordinary temperatures (e.g. sodium chloride or potassium chloride) or salts which are more soluble in cold water than in hot (e.g. sodium citrate). The quantity of salt used should be sufficient to give a highly concentrated or even saturated solution at the highest temperature reached during the kiering process. The products obtained according to our invention are easily ground and are indeed in many cases in such a condition as to require no grinding.
- 35 Any excess of solid salt may be recovered after the kiering treatment, and the concentration of the kiering liquor may be adjusted for further use by the addition of fresh kiering agent.
- 40 Our invention is applicable not only to the processes of the co-pending applications already mentioned but also to other processes in which cellulose ethers are submitted to a kiering treatment.
- 45 Our invention is illustrated but not limited by the following examples the parts and percentages of which are by weight.
- EXAMPLE 1.
- 50 100 parts of benzyl cellulose which has a viscosity of approximately 100 c.g.s. units in 10% solution in toluene-spirits mixtures (80 : 20) are kiered with 700 parts of 0.75% oxalic acid solution and 300 parts of sodium citrate for 3/4 hour at 30 lbs. per sq. in. The kiered mass is a discrete powder. It is washed free from acids and salts, and dried. The viscosity in 10% solution in toluene-spirits (80 : 20) is 5 c.g.s. units.
- EXAMPLE 2.
- 55 50 parts of ethyl cellulose with a viscosity of 250 c.g.s. units when measured in 10% solution in benzene, are kiered in a closed vessel with 575 parts of a solution containing approximately 0.95% of its weight of hydrochloric acid and 250 parts of commercial sodium chloride for a period of 30 mins. at a pressure of 25 lb. per sq. in. The resulting product in the kier is still in a loose non-caked condition, which can be easily ground in a mechanical mortar and washed free from impurities. The viscosity after purification

measures 5 c.g.s. units in a 10% solution in benzene.

EXAMPLE 3.

100 parts of a partially purified benzyl cellulose reaction mass, which contains about 5—13% of benzyl chloride, and a portion of which when purified gives a viscosity of 25 c.g.s. units in a toluene-spirit mixture (80 : 20) are heated with 1000 parts of water and 500 parts of commercial sodium chloride, for 3/4 hour at 25 lb. per sq. in. pressure.

The kiered product is a loosely cohering friable mass, which is easily ground in a mechanical mortar. When washed free from salts and dried, the product gives clear solutions with a viscosity of 0.5—2.0 c.g.s. units for a 10% solution in toluene-industrial spirit mixture (80 : 20).

In specification No. 342,391 as open to public inspection under Sect. 91 of the acts there is mentioned the use of acid salts in place of acids for the kiering of cellulose ethers. According to our invention on the other hand there is employed a quantity of "non-acid" salt entirely disproportionate to the amount of acid present, and we only claim the use of acid salt (such as might be regarded as present under these conditions) in the presence of large excess of non acid-salt, this large excess being necessary in order to obtain an easily ground product.

We are aware of Specification No. 333,902, and make no claim to anything claimed therein.

Having now particularly described and ascertained the nature of our said inven-

tion and in what manner the same is to be performed, we declare that what we claim is :—

1. Process for the manufacture of cellulose ethers of low viscosity by kiering a higher viscosity cellulose ether with dilute acids, characterised in that the kiering takes place in the presence of a quantity of a water-soluble non-acid salt sufficient to give a highly concentrated or even saturated solution at the highest temperature reached during the kiering process.

2. Process according to Claim 1, in which the acid used for kiering is produced in situ by the hydrolysis of an alkyl or aralkyl halide.

3. Process according to any of the preceding claims in which the salt used is so chosen that it has approximately the same solubility both at high and at ordinary temperatures, or is more soluble in cold water than in hot.

4. Process according to Claim 4 in which the salt chosen is sodium citrate, sodium chloride or potassium chloride.

5. Process for the manufacture of cellulose ethers of low viscosity substantially as described with reference to the examples hereinbefore set out.

6. Cellulose ethers of low viscosity whenever produced by the process of any of the preceding claims or by the obvious chemical equivalent of such process.

Dated the 6th day of March, 1931.

E. C. G. CLARKE,
Imperial Chemical House,
Millbank, London, S.W. 1,
Solicitor for the Applicants.