(54) IMPROVEMENTS IN OR RELATING TO
THE DEWATERING OF CLAYS

(71) We, ENGLISH CLAYS LOVERING POCHIN & COMPANY LIMITED, a British Company, of John Keay House, St. Austell, Cornwall, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the dewatering of clays by pressure filtration and more particularly but not exclusively is concerned with the dewatering of aqueous suspensions of white kaolin clays suitable for use as fillers in the manufacture of paper or the like product.

In the manufacture of paper or like product, there is generally incorporated in the fibrous pulp from which the paper or like product is formed a mineral filler the use of which *inter alia* reduces the cost of the product. One mineral filler which is used for this purpose is white kaolin clay which brings about an improvement in the opacity and printing properties of the paper. However, the white kaolin clay fillers conventionally used result in a reduction in the strength of a paper or the like product containing them; and it has recently been proposed that there should be used as the mineral filler for paper or like product a white kaolin clay having a particle size distribution such that the white kaolin clay contains not more than 18% by weight of particles smaller than 2 microns and not more than 15% by weight of particles smaller than 1 micron equivalent spherical diameter. This kaolin clay filler has an unusual particle size distribution in that there are present substantially fewer very small particles as compared with a conventional kaolin clay filler. In the course of preparing such a kaolin clay filler there is formed an aqueous suspension of the kaolin clay filler and it is convenient to complete the preparation of the kaolin clay filler by dewatering the aqueous suspension thereof to reduce the water content of the kaolin clay filler to less than 25% by weight and preferably to less than 20% by weight.

In the dewatering of the aqueous suspension of the kaolin clay filler precautions are taken to prevent as far as possible the formation of fine particles by fracture or shearing of coarser particles. The dewatering is therefore preferably carried out by pressure filtration at a pressure in excess of 150 psig. If a thermal drying step is used subsequent to the pressure filtration step the amount of mechanical work performed on the material in the thermal drying step should be as small as possible and the surface temperature of the material should not be allowed to exceed 120°C. Unfortunately it has been found that in practice it is not possible to eliminate completely from the kaolin clay filler fine particles nor to prevent completely the formation of such fine particles in the dewatering of the aqueous suspension and in other steps in the preparation of the kaolin clay filler.

It is found that when an aqueous suspension of a clay filler (such as the kaolin clay filler described above) which is substantially but not completely free of fine particles is dewatered in a pressure filter the cycle time (i.e. the total time taken for the pressure filter to perform all the operations necessary to form, dewater and discharge a filter cake) increases progressively; and when using a tube pressure filter of the type disclosed in British Patent Specification No. 1,240,465 the cycle time can increase from about 4 minutes with a new filter cloth to about 15 minutes, at which point the rate of production of filter cake is considered to be unacceptably low. The number of cycles performed in a tube pressure filter before the cycle time rises to this unacceptably high figure varies between about 100 and about 1000 whereas if a tube pressure filter is to be operated economically it is necessary for a filter cloth to remain

serviceable for much longer. Similar problems can arise with other types of pressure filters.

It has now been found that the increase in the cycle time is caused by penetration into the inter-filament voids of the filter cloth of fine particles. Although precautions can be taken in the production of a clay filler to keep the amount of fine particles as small as possible, it is not possible to eliminate all fine particles and a few fine particles are inevitably present; and it has been found that these few fine particles are not easily bound to the coarser particles by conventional flocculant (as is the case with a conventional kaolin clay filler having a larger proportion of fine particles) and are therefore free to penetrate the pores of the filter cloth.

According to the present invention there is provided a method of dewatering by pressure filtration an aqueous suspension of a clay having a particle size distribution such that it contains a minor proportion, being not greater than 20% by weight, of particles having an equivalent spherical diameter smaller than 1 micron, which method comprises treating the aqueous suspension of the clay, prior to dewatering thereof, with a water-soluble polyelectrolyte flocculant having a positive charge density (as hereinafter defined) greater than 1.0×10^{-3}, and thereafter dewatering said aqueous suspension by pressure filtration at a pressure in excess of 150 psig.

By the term "positive charge density" there is meant herein the total number of positive charges per molecule divided by the molecular weight of the flocculant, as measured by the Ostwald viscometer method. Preferably the molecule of the polyelectrolyte flocculant does not include any groups having negative charges or negative polarity (e.g. carboxyl or carbonyl groups) which would tend to counteract the positive charges.

The flocculants which are advantageously used in the method of the invention are polyelectrolytes containing quarternary nitrogen atoms in the polymer chain. The preferred flocculants are those obtainable by copolymerising epichlorohydrin and an aliphatic secondary amine, such flocculants having repeating units which can be represented by the general formula:
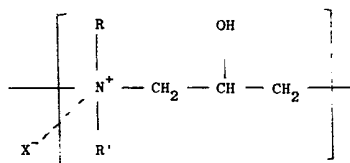
wherein R and R¹, which may be the same or different, are each hydrogen, methyl or ethyl and X is Cl, Br, I, HSO_4 or CH_3SO_4. These copolymers generally have a positive charge density in the range of from 4×10^{-3} to 9×10^{-3}, most usually in the range 6×10^{-3} to 8×10^{-3}. It is believed that with this type of polyelectrolyte flocculant the molecular weight of the flocculant may be important, and copolymers of the above formula having molecular weights (when measured by the Ostwald viscometer method) in the range of from 50,000 to 300,000 have been found to be very suitable. The quantity of this type of flocculant required is in the range from 100 to 3000 ppm. (parts by weight of flocculant per million parts by weight of dry clay). Adding more than the stated maximum dose can so saturate the clay with positive charges that the clay is one again deflocculated by virtue of the mutual repulsion of the positive charges.

In some circumstances it may be useful to use with the polyelectrolyte flocculant aluminium sulphate, provided that the pH of the aqueous suspension is in the range of from about 5.0 to 5.5. Aluminium sulphate $Al_2(SO_4)_3 . 18H_2O$, has a positive charge density of 1.0×10^{-3}.

The method of the present invention is especially useful in the dewatering, by pressure filtration at a pressure in excess of 250 psig, generally in a tube pressure filter of the type disclosed in British Patent Specification No. 1,240,465, of white kaolin clays having a particle size distribution such that they contain not more than 18% by weight of particles having an equivalent spherical diameter smaller than 2 microns and not more than 15% by weight of particles having an equivalent spherical diameter smaller than 1 micron.

The invention is illustrated by the following Examples.
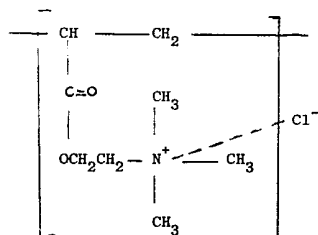
EXAMPLE 1

An aqueous suspension containing 27% by weight of a kaolin clay which had a particle size distribution such that 9% by weight consisted of particles having an equivalent spherical diameter smaller than 2 microns and 5% by weight consisted of particles having an equivalent spherical diameter smaller than 1 micron, was treated with 1000 ppm, based on the weight of dry kaolin clay, of a 50% by weight solution in water of a polymer having the repeating unit
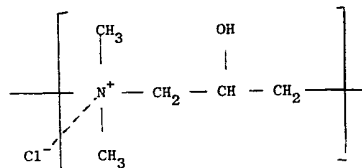
a positive charge density of about 7.3×10^{-3}, and a molecular weight in the range of from 200,000 to 300,000 in order to flocculate the kaolin clay. The suspension of flocculated clay was fed to a tube pressure filter of the type described in British Patent Specification No. 1,240,465 and a large number of cycles were performed; the rate of production of filter cake in pounds per hour was measured at intervals. The filter element of the tube pressure filter comprised a 7 oz. per square yard "nylon" filter cloth with a "Terylene" felt backing cloth. (The word Terylene is a Trade Mark). The pH of the feed suspension remained constant at 4.3 throughout and for approximately the first 2000 cycles the maximum hydraulic fluid pressure was 1500 psig, for the next 4500 cycles the maximum hydraulic fluid pressure was 1100 psig, and for the remaining cycles the maximum hydraulic fluid pressure was again 1500 psig. At the beginning of the sequence of cycles, when the filter cloth was new, the rate of production of filter cake was 410 lb/hr. and it remained substantially at the same level until about 8,300 cycles had been completed, at which point the rate of production began to fall slightly reaching 320 lb/hr. after 11,300 cycles when the run was terminated. As a comparison a run was carried out under the same conditions as above but using no flocculant in the kaolin clay suspension. At the beginning of the run, when the cloth was new, the rate of production of filter cake was 650 lb/hr. But this fell rapidly to 180 lb/hr, in 1000 cycles.

EXAMPLE 2

An aqueous suspension containing 27% by weight of a kaolin clay of the same type as was used in Example 1 was treated with 150 ppm, based on the weight of dry kaolin, of a cationic copolymer obtained by hydrolysing about 10% of the repeating units of a polyacrylamide to acrylic acid and then esterifying the acrylic acid groups with an aliphatic alcohol containing a quaternary ammonium group. The esterified acrylic acid groups had the following structure:

$$
\left[\begin{array}{c} \overset{|}{\underset{|}{CH}} \text{————} CH_2 \text{————} \\ C=O \\ | \\ OCH_2CH_2 - N^+ \begin{array}{c} CH_3 \\ \diagup \\ \diagdown \\ CH_3 \end{array} CH_3 \end{array} \right] Cl^-
$$

The positive charge density of the copolymer was about 1.2×10^{-3} and the molecular weight was about 5×10^6. The flocculated clay suspension thus obtained

was fed to the same tube pressure filter using the same cloths as in Example 1, and the change of rate of production of filter cake with the number of cycles performed was observed. The pH of the feed suspension remained constant at about 3.0 throughout and the maximum hydraulic fluid pressure used was 1500 psig. When the filter cloth was new the rate of production of filter cake was 600 lb/hr. but this fell steadily at first until after 750 cycles the rate of production was 400 lb/hr. The rate of production then remained substantially constant at this level until, after 2,300 cycles, the filter cloth burst possibly because of the consistently low pH requirement.

EXAMPLE 3

An aqueous suspension containing 26% by weight of a kaolin of the same type as was used in Example 1 was treated with sufficient aluminium sulphate to provide 0.6 mg of aluminium per g. of kaolin, sufficient sodium carbonate to raise the pH to 5.5 and 150 ppm, based on the weight of dry kaolin, of the same copolymer as was used in Example 2 in order to flocculate the kaolin.

The flocculated suspension was fed to the same tube pressure filter using the same type of filter cloth as in Example 1, and the change of production of filter cake with the number of cycles performed was observed. The pH of the feed suspension varied between 5.0 and 6.0 and the maximum hydraulic fluid pressure used was 1500 psig. When the filter cloth was new the rate of production of filter cake was 605 lb/hr. but this fell steadily at first until after 1500 cycles the rate of production was 400 lb/hr. The rate of production then remained substantially constant at this level until 2,900 cycles had been completed when the run was terminated.

EXAMPLE 4

A kaolin clay of the same type as was used in Example 1 was formed into an aqueous suspension containing 12% by weight of solids. Samples of this suspension of volume 15.7 ml (i.e. containing 2.0 g of dry kaolin clay) were placed in test tubes and to each test tube there was added a different quantity of the polymeric flocculant described in Example 1. The contents of each test tube were mixed by covering the mouth of the test tube and rapidly inverting the tube several times. The flocculant was added to the test tubes as a solution containing 0.1% by weight of the polymer by a 1 ml pipette graduated in 0.01 ml. After mixing, the contents of each test tube were allowed to stand for 30 hours, after which time the volume of flocs was determined for each test tube by measuring the height of

the interface between flocs and supernatant liquid above the bottom of the tube. A large volume of flocs indicates the formation of large, s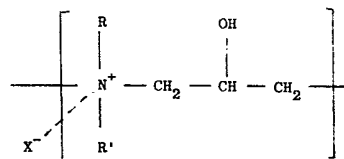trong, open flocs which are most suitable for highpressure filtration. A visual observation was also made of the clarity of the supernatant liquid. The results obtained are set forth in the following Table.

Quantity of flocculant added (ppm)	Depth of flocs (mm)	Clarity
0	23	Cloudy
50	33	Cloudy
100	38	Slightly cloudy
200	42	Very slightly cloudy
300	47	Very slightly cloudy
400	46.5	Very slightly cloudy
500	54	Clear
600	54	Clear
700	56	Clear
800	58	Clear
900	59	Clear
1000	61.5	Clear
2000	59.0	Clear
3000	50	Very slightly cloudy
5000	45	Cloudy

In the tube pressure filter it was found that the cloth blinded very quickly when it was attempted to dewater a suspension of kaolin clay containing less than 100 ppm or more than 3000 ppm of the flocculant. Best results were obtained with this flocculant when the quantity used was from 500 to 2500 ppm (parts by weight of flocculant per million parts by weight of dry kaolin clay).

WHAT WE CLAIM IS:—

1. A method of dewatering by pressure filtration an aqueous suspension of a clay having a particle size distribution such that it contains a minor proportion, being not greater than 20% by weight, of particles having an equivalent spherical diameter smaller than 1 micron, which method comprises treating the aqueous suspension of the clay, prior to the dewatering thereof, with a water-soluble polyelectrolyte flocculant having a positive charge density (as hereinbefore defined) greater than 1.0×10^{-3}, and thereafter dewatering said aqueous suspension by pressure filtration at a pressure in excess of 150 psig.

2. A method according to claim 1, wherein the water-soluble polyelectrolyte flocculant does not include any groups having negative charges or negative polarity.

3. A method according to claim 1 or 2, wherein the water-soluble polyelectrolyte flocculant contains quarternary nitrogen atoms in the polymer chain.

4. A method according to claim 3, wherein the polyelectrolyte flocculant is one obtainable by copolymerising epichlorohydrin and an aliphatic secondary amine, said flocculant having repeating units which can be represented by the general formula:

$$\left[\begin{array}{c} R \\ | \\ \underset{\underset{\displaystyle R^1}{\displaystyle |}}{\overset{+}{N}} \\ X^- \end{array} - CH_2 - \overset{\overset{\displaystyle OH}{\displaystyle |}}{CH} - CH_2 - \right]$$

where R and R^1, which may be the same or different, are each hydrogen, methyl or ethyl and X is Cl, Br, I, HSO_4 or CH_3SO_4.

5. A method according to claim 4, wherein the molecular weight of the flocculant is in the range of from 50,000 to 300,000 (as measured by the Ostwald viscometer method).

6. A method according to claim 4 or 5, wherein the amount of flocculant employed is in the range of from 100 to 3000 ppm (parts by weight of flocculant per million part by weight of dry kaolin clay).

7. A method according to any one of claims 1 to 6, wherein the clay is a white kaolin clay which is dewatered by pressure filtration at a pressure greater than 250 psig

and which contains not more than 18% by weight of particles smaller than 2 microns equivalent spherical diameter and not more than 15% by weight of particles smaller than
5   1 micron equivalent spherical diameter.

    8. A method according to claim 1 of dewatering by pressure filtration a kaolinitic clay, substantially as described in any one of the foregoing Examples.

10   9. A clay whenever dewatered by the method claimed in any one of the preceding claims.

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