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(54) Title: A PROCESS FOR DE-INKING PAPER PULP

(57) Abstract

The de-inking of paper pulp is rendered more efficient and capable of producing a high quality recycled paper for printing purposes by the addition of surfactants having a chemical character similar to surfactants naturally present in the pulp. The surfactants may be in the form of hemicellulose which include polysaccharides and a small proportion of side-chain carboxyl groups. Methods for the manufacture of artificial surfactants similar to the surfactants present in the pulp are described, such as surfactants being co-polymers made for example from vinyl acetate and acrylic or maleic acid, the conversion being completed by transesterification with methanol in the presence of sodium methoxide.

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A PROCESS FOR DE-INKING PAPER PULP.

This invention relates to a process for de-inking paper pulp and to materials used in the process.

With the continued depletion of world supplies of raw materials and consequent increased costs, general interest in recycling paper has increased substantially of recent years. While the problem of de-inking the pulp is not particularly acute where the recycled product is to be used for packaging and other non-print applications, where the recycled product involves subsequent printing, efficient de-inking becomes essential.

Two de-inking processes currently in use employ aqueous alkaline suspensions of paper fibre as the feedstock, and one process involving use of large quantities of water is only practicable where large quantities of fresh water are readily available. The other process involves flotation. The basic flotation process is simple and merely calls for disintegration of the waste paper in a dilute alkaline solution of a sodium soap. The resultant pulp is generally diluted to a consistency of about one percent solids and calcium ions are then added to insolubilize the sodium soap. This mixture is stirred and aerated so that the calcium soap particles, together with the ink, are carried to the surface of the liquid by the air bubbles and the floating scum or foam is then removed by any suitable conventional means. Consideration in more detail of the flotation process indicates that the following requirements must be met:

1. The action of pulping the waste material must detach the ink particles from the fibres and since inks are held to paper by purely physical forces the mechanical pulping action is generally adequate to have this effect and can be enhanced by surfactants.
2. The detached ink particles must be emulsified to a sufficient extent to prevent redeposition on the

fibres but at the same time, the emulsions produced must not be so stable that carrier particles required to raise the ink particles to the surface have difficulty in attracting the ink from the emulsions.

3. The carrier itself must have the required affinity for the ink and be suitable for rapid transport to the surface of the pulp by the air and the carrier and ink must form a foam or scum at the surface.
4. The foam must have characteristics suited to efficient mechanical removal in particular it should not incorporate significant quantities of fibres, since otherwise the overall efficiency will be reduced.

Flotation de-inking as currently used in practice, indicates that the complex processes are finely balanced and unsatisfactory results can easily occur if any imbalance occurs in these processes. It has been found that the level of calcium ions which it is necessary to add to the pulp much exceeds that required to insolubilize the sodium soap and it is also found that the addition of synthetic anionic and non-anionic surfactants in addition to the added sodium soaps serve to reduce the speed with which the carrier particles can transport the ink to the surface foam. Also the production of foam is dependant upon the pH value and a minimum level of 8-8.5 is generally needed for satisfactory results.

The fact that the addition of any synthetic surfactants is not helpful to the efficient de-inking process is anomalous because the soap is present in an insolubilized form and cannot therefore play its normal roles. It is therefore to be concluded that the surfactants required for efficient de-inking are present in the pulp itself and the invention is based on the addition to the pulp of synthetic surfactants having a character and composition generally similar to the surfactants naturally present.

According to the present invention there is provided a process for de-inking paper pulp comprising the addition to the pulp of a surfactant having a character and composition generally similar to surfactants naturally present in the paper.

Experimental work shows that using identical flotation techniques, different papers used in the pulps will give substantially different efficiencies of de-inking. For example, papers based on unbleached sulphite pulp from integrated production facilities were much more easily de-inked than those derived from market sulphite, sulphate or mechanical pulps. It was found that alkaline extracts of integrated sulphite pulps improved the efficiency of de-inking to a marked extent. Experiments showed that the required surfactant material was soluble in alkaline but relatively insoluble in acid situations.

Further experimental work shows that an extract of the sulphite-insoluble hemicellulose fraction of wood contained the active ingredient. The hemicellulose fraction is a mixture of polysaccharides based mainly on xylose and a small proportion of side-chain carboxyl groups. This hemicellulose is soluble in alkaline but insoluble in acid and is therefore found only in pulps prepared under acid conditions.

It follows from this experimental work that the sodium soap merely acts as a carrier when insolubilized with calcium and the stabilization of the ink particle emulsion and the surfactant foam is effected by calcium salts of the hemicellulose fraction. Hence, in order to obtain the best results it is necessary to use alkaline solutions in order to dissolve the hemicellulose and to use a relatively high level of calcium ions in order to form the calcium salts of the hemicellulose compound.

With regard to the use of synthetic foaming agents added to the flotation process, those currently used for example fatty alchohol ethoxylates, have the disadvantage that they hinder efficient surface removal of ink and moreover, lead to high fibre losses due to the collection of fibre in the foam structure under the conditions of use, In contrast, naturally-occurring foaming agents found in sulphite pulps produce stable foams and do not, in general, induce foam collection of fibre. These natural foaming agents are believed to be xylan polymers containing methylated glucuronic acid side-chains but the quantity available in the natural pulp is not always adequate and/or cannot readily be controlled.

The added material intended both as a surfactant and as a foaming agent should resemble natural hemicelluloses as far as possible and thus contain a high proportion of hydroxyl and a low proportion of carboxyl groups in a linear polymeric structure.

One suitable co-polymer is made from vinyl acetate and acrylic or maleic acid and the co-polymer is made by removing acetate residues by transesterification with methanol in the presence of sodium methoxide (made by adding sodium to methanol). It is found that such co-polymers have specific properties necessary for foaming at high calcium levels (say 250 p.p.m) in alkaline solutions.

The manufacture of synthetic co-polymers suitable for carrying out the process in accordance with the invention will now be described.

50 gm. of vinyl acetate monomer was dissolved in 100 ml. of toluene and subsequently hydroxy-propyl methacrylate and maleic acid or acrylic acid were added to the solution to form a co-polymer from the three monomers. Azo-bis-iso-butyronitrile (hereinafter referred to as "AZBN") was used as an initiator for the co-polymerization. In the quantities used 0.3 gm. was sufficient. As an alternative benzoyl peroxide could be used but gave slightly less good results.

The solution was then heated under reflux for three hours after which period it had become more viscous. After allowing the solution to cool to some extent, petroleum ether (60-80° fraction, approximately 200 ml.) was then added.

The mixture was then stirred by hand, and the polymer separated out as a gel. The liquid was decanted off and discarded. Approximately 250 ml. of methanol was then added and the gel dissolved by heating and stirring. When all the polymer had dissolved, a small amount of sodium methoxide was added. The solution was then heated under reflux for half an hour, at the end of which time the polymer had precipitated. The polymer was then filtered off. At this stage, the polymer was swollen due to methanol trapped in the structure. After drying in an oven overnight, the polymer had shrunk to a very small fraction of its original volume. It was then crushed to powder.

In some of the preparations, deviations were made from this general method: in the first process, for example, the acid was added at the start, but in some preparations, it was added in a solvent dropwise throughout the reaction. When the intermediate product was reluctant to dissolve in the methanol, a chain terminator, such as dodecyl mercaptan or iso-propyl alcohol, was added at the start of the reaction to keep the molecular weight of the polymer comparatively low. For the same purpose 2 ml. of concentrated sodium hydroxide solution were used instead of the methoxide in the latter stage in some examples, and in others, it was necessary to add a little petroleum ether (60° - 80° fraction) to precipitate the final product. In one example, a little glacial acetic acid and a little water were needed to throw the product out.

Pure poly (vinyl alcohol), was also prepared so that its properties in the flotation de-inking system could be compared with the co-polymers.

The polymers prepared were characterised by the following two methods:

a) By infra-red spectroscopy: the polymer was dissolved in water and a film cast on a silver chloride plate. The water was evaporated in an oven. The spectrum was run on a Perkin-Elmer 157G grating infra-red spectrometer.

b) A weighed amount of each polymer was dissolved in 250 ml. of methanol and the solution was titrated with standardised potassium or sodium hydroxide, using phenolphthalein as indicator. The percentage by weight of acid monomer in the polymer was then calculated from this titration.

These two tests were also performed on a sample of the intermediate which was taken before the methanol was added.

In accordance with the general preparation methods referred to, the following synthetic polymers were made:

<u>Example 1</u> Reactants: 50gm. vinyl acetate, 30gm. hydroxypropyl methacrylate, 5gm maleic acid, 20ml. iso-propanol. Solvent: 100ml toluene. Initiator: 0.3gm. AZBN. The reactants were heated at 85°C under reflux for three hours. The isolation of the intermediate and the methanolysis were then performed and the product was precipitated by the addition of petroleum ether. Yield 21gm. Acid content of intermediate: 15.1% and of the product: 6.2%.

<u>Example 2</u> Reactants: 50gm. vinyl acetate, 30gm. of hydroxypropyl methacrylate 6.9gm. of acrylic acid, 20ml. of isopropyl alcohol. Solvent: 100ml. of toluene. Initiator: 0.3gm. of AXBN. This mixture was heated at 86°C under reflux for 2¼ hours. The general method was then followed and petroleum ether was used to precipitate the product. Yield 30gm. Acid content of intermediate: 19.2% of product: 13.7%.

<u>Example 3</u> Reactants: 50gm. of vinyl acetate, 30gm of hydroxy-propyl methacrylate, 2gm. of acrylic acid, 20ml. of iso-propyl alcohol. Solvent: 100ml. of toluene.

Initiator: 0.3gm. of AZBN. The reactants were heated under reflux at 83°C for two hours. The product prepared by the general method proved difficult to extract: on adding toluene and petroleum ether still no product was precipitated. A little glacial acetic acid and a little water were added and the product separated slowly with stirring. Yield 5.6gm. Acid content of intermediate: 9.6% of product: 9.7%.

Example 4 Reactants: 50gm. of vinyl acetate, 30gm. of hydroxypropyl methacrylate, 5gm. of maleic acid, 10gm. of trichloroacetic acid. Solvent: 100ml. of toluene. Initiator 0.3gm. AZBN. These were heated under reflux at 90°C for two hours. The product was then prepared as in the general method. Yield 6gm. Acid content of product: 10.6%

Example 5 Reactants: 50gm. of vinyl acetate, 25gm. of methyl acetate, then 0.15gm. of maleic acid dissolved in 25gm. more of methyl acetate added dropwise. Initiator: 0.3gm of AZBN. The mixture was heated under reflux for one hour while the acid was added, and the heating was continued for a further hour. Approx. 20ml. methanol and 1ml. of 40% sodium hydroxide solution were then added. The mixture was heated under reflux for 30 minutes, at the end of which time the product had precipitated out. This was filtered and washed with acetone before being dried in an oven. Yield 6.7gm. Acid content of product: 2.0%.

Example 6 Reactants: 50gm. of vinyl acetate, 25gm. of methyl acetate, Initiator: 0.3gm. of AZBN. These reactants were heated under reflux for four hours. During the first two hours the following were run in dropwise: 25mg. of methyl acetate, 0.15gm. of maleic acid, 0.2gm of AZBN. After four hours approximately 20 ml. of methanol, and 1-2ml. 40% sodium hydroxide solution were added. This produced a considerable amount of heat and some of the solution blew out of the top of the condenser. The solution was cooled in an ice bath before heating under reflux for 30 minutes.

Yield 6gm. Acid content of product 2.1%.

Example 7 Reactants: 50gm. of vinyl acetate, 25gm. of methyl acetate and then 0.1gm. acrylic acid and 25gm. methyl acetate. These added dropwise over the first three hours. Initiator: 0.3gm. AZBN. The mixture was heated under reflux for four hours before being cooled in an ice-bath. 200ml. of methanol and 2ml. of 40% sodium hydroxide solution, were added. The mixture was then heated to reflux for half an hour, the product was precipitated and was filtered and dried. Yield 4.6gm. Acid content of product: 1.9%.

Example 8 Reactants: 50gm. of vinyl acetate, 25gm. of methanol, 25gm. of methyl acetate, then 0.2gm acrylic acid and 25gm methanol 25gm dropwise. Initiator: AZBN (0.1gm at start, then two additions, each of 0.1gm., after one hour as for product 7. Yield: 7gm. Acid content of product: 2.1%.

Example 9 Reactants: 50gm. of vinyl acetate. Solvent: 100ml of methyl acetate. Initiator: AZBN 0.3gm. These reactants were heated under reflux for four hours. After two hours, 0.3gm. of AZBN and 20ml. of toluene were added. The solution was then cooled somewhat. and approximately 250ml. of petroleum ether were added with stirring. The liquid was decanted off and discarded. 300ml of methanol was added with heating and stirring to dissolve the polymer. After adding some methoxide the solution was heated under reflux for half an hour. The product was filtered and dried in the usual way. Yield 10.5gm.

Use of the examples set out above for de-inking newsprint will now be described in relation to the general method employed.

The first stage was to pulp the sample of newsprint : this was performed in a standard pulp evaluation disintegrator. 2 litres, 40°-45°C of warm water, 0.7gm. of the polymer, 1.0gm. of sodium hydroxide and 4.0gm. of sodium metasilicate were added to the pulper. The mixture was then stirred for a count of 500 on a counter fitted to the pulper to ensure that the polymer had dissolved; each unit on the counter is equivalent to 25 revolutions of the stirrer shaft - 50 revolutions per second. 2ml. of 100 volume hydrogen peroxide solution was then added. The solution was further agitated. 2gm. of calcium chloride was then added with stirring. 70gm. of newsprint was added, the counter was set at 3,000 and the disintegrator started. The contents of the pulper were checked after 100 on the counter, to see if there had been any separation of ink from the pulp.

During this process, 1.5gm. of tallow soap was dissolved in 200-300ml. of water on a stirrer/hot plate. 2.0gm. of calcium chloride and 1.0gm. of sodium hydroxide were placed in a bucket with some hot water to dissolve them.

The contents of the pulper were again checked and then transferred to the bucket. The pulper was rinsed with hot water, which was added to the contents of the bucket. The latter was then made up to the volume of the flotation tank with cold water.

The flotation tank was a cylindrical cell of 7.5 litres capacity, constructed of stainless steel, which incorporated a multi-pored base bubbler attached to a pressurised air supply, and an overhead stirrer with a butterfly blade system.

The soap solution was placed in the flotation tank and the pulp transferred to it. The air flow was adjusted to a rate of 0.95 litres/min. and the stirrer motor was switched on, running at a rate of approximately 1,200 revolutions/min. The froth was removed by manual scraping with a palette knife from the top of the tank for 20 minutes.

The froth removed was checked to see:

a) the extent of fibre removal and

b) whether the ink was being removed as large or small particles, or not at all.

The de-inked pulp was then formed into handsheets: a sample of 1,500ml. was taken out of the flotation tank (through the tap on the side). The water was then drained off in a 60-mesh sieve and the resultant pulp was then thickened, most of the remaining water being pressed out. The pulp was then re-diluted to 1,500ml.

The diluted pulp was then made into three handsheets, each of 500ml. using a filter tank and a press. In each case, some water was run into the filter tank and 500ml. of pulp were poured in at the same time. The tank was then emptied, leaving a film of paper on the mesh. Two sheets of blotting paper and then a 7" diameter metal disc were placed on top of this. Then using a heavy, metal roller, the sheet was rolled seven times. The blotters plus sample were placed on the press for the first pressing: two blotters were placed on the press, then the two blotters plus sample (sample facing upwards), and then a 6" diameter metal plate. This was repeated for the second and third samples, and then a further two blotters were placed on top. The first pressing lasted for four minutes, then the samples were prepared for the second pressing: all the blotters used in the first pressing were discarded and the metal plate and sample were removed together in each case. For the second pressing, each sample plus metal plate was placed on top of two blotters (sample upwards) on the press. Two blotters were placed on top of all and the second pressing (two minutes) was performed. The samples were then left to dry overnight.

A number of points were monitored throughout the whole flotation de-inking process. At the pulping stage, the state of the pulp in the pulper was checked twice, after 100 on the counter and at the end, to see how clean the pulp was and if the ink had separated at that stage. During the transfer from pulper to flotation tank, it was noted whether any ink had stuck to the sides of the bucket.

The state of the foam in the tank was also noted, i.e. whether the bubbles were large or small (heavy or light foam), whether the ink was removed as large or small particles, how much fibre was being removed. This was checked by putting a sample of foam on to a blotter.

The finished handsheets were examined both visually and spectrophotometrically. Reflectance values at 457nm. were obtained using a 90° incident beam against a standard of barium sulphate. The rougher side of the handsheet (the non-wire side) was used for this measurement. A reflectance value of about 50 was considered very poor, and a value of 56 or more was very good.

The method outlined above and the tests applied were carried out with each Example hereinbefore described. The results are conveniently summarized in the following table for each example:

	Differences from general	Contents of pulper	Foaming in tank	Handsheets (Reflectance)
Example 1				
Trial 1	No polymer added	Clean (after 100 on the counter), some ink stuck to sides of the bucket at the end of trial.	Small, light bubbles slow to form, some fibre, not all ink removed.	Fair (50.6)
Trial 2	None	Slight separation of ink.	Inky foam, slightly quicker to form than trial 1. Most ink seemed to be taken out, extra 1gm. NaOH improved foaming.	Fair (51.2)
Trial 3	Extra 0.5gm. NaOH in flotation.	Slight separation of ink.	Good foaming, largish, light bubbles, quite quick to form, little fibre loss. Ink taken out quite quickly.	Quite good (54.4)
Trial 4	1.5gm. NaOH in each stage	Slight separation of ink at 100 on the counter, cleaner at end of trial.	Good foaming, largish, light bubbles, ink came off quickly, foam quicker to form than in trial 3. Little fibre loss.	Good (56.3)
Trial 5	60gm. newsprint, 15m. magazines, no polymer used. 1.5gm.NaOH in each stage	Inky scum at top after 100 on the counter, same at end, some ink stuck to sides of container.	Large, heavy bubbles quick to form; good foaming. Considerable ink, but little fibre taken out.	Quite good (53.9)

	Differences from general	Contents of pulper	Foaming in tank	Handsheets (Reflectance)
Trial 6	As Trial 5, but with polymer	Considerable inky scum separated.	More foam than trial 5 quicker formation of same type of foam. Most ink removed by 15 minutes.	Quite good (55.0)
Trial 7	1.5gm. NaOH in flotation stage. Soap added in pulper.	Inky scum on top after 100 on the counter, ink particles separated at the end of the trial.	Very good foaming, large heavy bubbles, most of the ink removed by 10 minutes, very little fibre removed.	Good (56.4)
Trial 8	No polymer, soap was placed in pulper. 1.5gm. NaOH in each stage.	Considerable inky scum after 100 on the counter, but only traces of ink at end.	Again good foaming, most ink removed by 15 minutes, foaming slower and less than trial 7. Little fibre loss.	Quite Good (53.3)
Trial 9	No peroxide, soap in pulper 1.5gm. NaOH in each stage.	Inky scum separated out.	Comparable to trial 8.	Fair (49.9)
Trial 10	Aged w/o newsprint used; 1.5gm NaOH in each stg.	Clean	Good foaming, small bubbles removed considerable ink at start but little at end. Some fibre removed.	Fair (52.2)
Trial 11	0.15gm. polymer used; 1.5gm NaOH in each stage.	Reasonably clean	Quite good foaming, quite a lot of ink but little fibre removed.	Quite good (52.7)

	Differences from general	Contents of pulper	Foaming in tank	Handsheets (Reflectance)
EXAMPLE 2				
Trial 1	No polymer used. 1.5gm. NaOH in pulping stage.	Slightly inky scum separated.	Not very good; seemed to remove little ink. Some fibre removed.	Fair (52.0)
Trial 2	1.5gm. NaOH in pulping stage	Slight foaming on top	More foam than trial 1, did not seem to remove a lot of ink. Some fibre loss.	Good (54.5)
Trial 3	None	Slight inky scum separated	Not very good some ink removed as small particles, little fibre removed.	Fair (52.3)
Trial 4	4gm. $CaCl_2$ in flotation stage	Reasonably clean.	Not very great. Some ink removed at first, little at end of trial. Some fibre loss.	Quite good (53.3)
Trial 5	4gm. $CaCl_2$ and 1.5gm. NaOH in flotation stage	Reasonably clean, a little foam.	Quite good foaming and ink removal. Some fibre removed.	Good (55.6)
Trial 6	6gm. $CaCl_2$ and 2gm. NaOH in flotation stage	Reasonably clean	Good foaming. Good removal of ink as fine particles. Little fibre removal.	Good (56.8)
EXAMPLE 3				
Trial 1	No polymer used. 1.5gm. NaOH in stage.	Quite clean	Quite good foaming, but not good removal of ink. Some fibre removed.	Good (55.4)

	Differences from general	Contents of pulper	Foaming in tank	Handsheets (Reflectance)
Trial 2	0.7gm. intermediate used 1.5gm. NaOH in each stage.	Much the same as trial 1.	Very light foam but ink seemed to be removed. Pulp at end of trial was grey. Little fibre loss.	Quite good (52.7)
Trial 3	1.5gm. NaOH in each stage	Slight foam at top.	Negligible. 3gm. $CaCl_2$ and 1gm. NaOH added then foaming quite good but light, seemed to remove ink quite well. Some fibre loss.	Fair (51.2)

EXAMPLE 4

Trial 1	1.5gm. NaOH used in each stage. 0.7gm. intermediate used.	Reasonably clean after 100 on the counter; large particles of ink separated at the end of trial.	Poor, unstable and slow to form foam. Some fibre removed. Little ink being removed towards the end of trial.	Good (55.1)
Trial 2	1.5gm. NaOH in each stage.	Quite clean	Rather poor foaming - slow to form and unstable. Considerable ink removed at start still removing at end. Little fibre loss.	Quite good (54.7)
Trial 3	Also 2.1gm. polymer in flotation stage. 2gm. NaOH in each stage	Some ink particles separted after 100 on the counter; reasonably clean at end.	Very poor, 2gm. NaOH + 8gm. $CaCl_2$ added then foamed very well, but did not seem to remove much ink. Little fibre loss.	Fair (51.5)

	Differences from general	Contents of pulper	Foaming in tank	Handsheets (Reflectance)
EXAMPLE 5				
Trial 1	0.25gm. polymer used. 1.5gm NaOH in each stage.	Some foam at top.	Very good; considerable foam and seemed to remove ink well. Some fibre loss. Foam became wet towards end.	Quite good (54.2)
Trial 2	1.5gm. NaOH in each stage.	More foam at top than trial 1.	Much the same as trial 1 but seemed to remove ink more efficiently; foaming better near end.	Good (55.6)
Trial 3	1.5gm. NaOH in each stage.	Considerable foam on top at end.	Quite good, ink removed as fine particles. Ink still coming off at end. Some fibre removed.	Quite good (53.4)
EXAMPLE 6				
Trial 1	Soap in pulper. 1.5gm. NaOH in each stage.	Light foam on top.	Excellent. Ink removal clean and finely divided. Ink finished coming off after about 10 minutes.	Good (54.8)
Trial 2	As trial 1, but no $CaCl_2$ added.	Some ink particles separating towards end.	Foam-free particulate scum. 4gm. $CaCl_2$ added: then foam generation still much lighter than trial 1. Ink still highly particulate.	Excellent (60.2)

	Differences from general	Contents of pulper	Foaming in tank	Handsheets (Reflectance)
Trial 3	Soap in pulper. 0.5gm. $CaCl_2$ in pulper; none in flotation stage.	Some particles of ink separated. Ink separated on dilution.	Poor: all the ink came off in about 10 minutes after 6gm. $CaCl_2$ added then quite good foaming. Time taken 15 minutes.	Very good (56.2)
Trial 4	As trial 3, but 0.75gm. $CaCl_2$ used.	Much the same as trial 3.	Poor: all the ink came off in about 5 minutes after 6gm. $CaCl_2$ added then quite good foaming. Time taken 10 minutes.	Very good (57.1)
Trial 5	As trial 3, but 1.0gm. $CaCl_2$ used.	Much the same as trial 3.	Much the same as trial 4.	Very good (56.7)
<u>EXAMPLE 7</u>				
Trial 1	1.0gm. $CaCl_2$ used, in each stage, soap in pulper.	Inky scum separated. Coarse inky scum on dilution.	Very light white foam - did not seem to take much ink out.	Good (54.4)
Trial 2	1.5gm. NaOH in each stage	Inky scum on top after 100. At end quite clean.	Quite good, took ink out quite well as fine particles. Some fibre removed.	Poor (50.2)
<u>EXAMPLE 8</u>				
Trial 1	1.5gm. NaOH in each stage.	Considerable inky scum after 100 on the counter, less at end of trial.	Good, ink removed as fine particles, some fibre loss. Little ink being removed but still good foaming at end of trial.	Fair (52.9)

Page 17a to follow

It should be noted that the reflectance of a handsheet is only one measure of its appearance; it may be more or less speckled or off-colour and as a result the reflectance may not measure the appearance exactly.

Page 18 to follow

The products prepared before that of Example 1 were stages in developing a linear polymeric chain with a high proportion of -OH groups and a low proportion of carboxyl groups. It was, of course, important that the intermediate product in the process should dissolve fairly readily in methanol when stirred and heated. The final product should dissolve in warm water fairly easily and should froth freely in both alkaline and neutral solutions.

The polymers were characterised by their acid numbers, the amount by weight of acid monomer as a percentage in the product, and by their infra-red spectra. In practice the infra-red spectra appeared very much the same in all cases. All the polymers showed a strong absorbance at a wavelength of about 3500cm^{-1}; this is characteristic of the -OH group. There was a peak in the spectra of the intermediates which became almost negligible in the spectra of the final products. This peak (at a wavelength of 1575cm^{-1}) did not appear in any of the spectra of the monomers on their own, but it did appear in the pure poly (vinyl alcohol) spectrum. It could perhaps be attributed to a carboxyl group. One peak definitely attributed to a carboxyl group (at a wavelength of 1400cm^{-1}) appeared in the spectrum of the intermediate and then appeared much weaker in that of the product. There was a peak at a wavelength of 1727cm^{-1} which was attributed to an ester carbonyl group, but the intensity was approximately the same in the spectra of the intermediate and the product.

Example 1, (acid content 6.2%), had twice the level of hydroxypropyl methacrylate at the start as compared to earlier Examples, not described. It was found that a higher sodium hydroxide level in each of the pulping and flotation stages gave a much better paper product. These levels were generally used in the production of all handsheets. The best results were obtained by trial 7, with 0.7gm. polymer and the soap added in the pulper, which gave very good handsheets with a reflectance of 56.4. The trial was repeated with no peroxide and gave poor handsheets with a reflectance of 49.9. This shows that the peroxide is necessary; but merely adding a large amount of bleach to obtain good handsheets does not give adequate results. Also, if the soap is added to the pulper instead of to the flotation tank, the ink tends to separate in the pulper and sticks to its side and to the bucket during transfer to the flotation tank.

Example 2, (acid content 13.7%), was prepared similarly to Example 1, except that acrylic acid was used instead of maleic acid. This also gave quite good results, but only after the addition of extra calcium chloride in the flotation stage.

Example 3, (acid content 9.7%), contained a smaller amount of acrylic acid than Example 2. This proved particularly difficult to isolate, and after that it gave a very poor performance as de-inking additive.

Example 4 including maleic acid as opposed to acrylic acid, and also some trichloroacetic acid which might become trapped in the polymer structure, was then prepared. De-inking trials were then run with both the product and the intermediate and both gave very poor results. Models for maleic and acrylic acids when incorporated in a co-polymer are succinic and propionic acids, respectively. pK_a for propionic acid is 4.87, and for succinic acid pK_a (1) is 4.16 and pK_a(2) is 5.61. From these values it is seen that the two acids are comparable in acidity with each other.

Due to the poor performance of these "high-acid" polymers only a trace of acid was added to the co-polymer of later Examples. Both Examples 5 and 6 had a small amount of maleic acid added as a solution in methyl acetate from a dropping-funnel. To produce Example 5 the first stage was heated under reflux for two hours whereas this polymerisation lasted four hours in Example 6. Example 5 (acid content 2.0%), produced quite good results; it was interesting to note that 0.7gm. of additive produced the same amount of foam as 0.25gm., but removed the ink more efficiently. Example 6, (acid content 2.1%), gave excellent results, but it was thought that the calcium level was too high and some trials were performed with different calcium levels. These produced particularly good handsheets; probably the best results so far have come from Example 6.

Example 7 and 8 were much the same as Example 5 and 6 but contained small amounts of acrylic acid (added dropwise). Neither of these products, though, proved to be as good an additive as Example 6. Example 7, (acid content 1.9%), did not produce a large amount of foam and little ink seemed to be removed, though the handsheets were reasonable. In the second trial, though foaming well, poor handsheets resulted. Example 8 (acid content 2.1%), gave a good foam but poor handsheets were produced. Generally, ink removal was not satisfactory.

From the foregoing results it will be apparent that there was a definite improvement in foaming and ink removal in general when using one of the co-polymers in accordance with the invention in the flotation de-inking process as opposed to using no additive at all.

The polymers which performed the best in flotation de-inking as an additive were those with some acid present in the chain, but not too much. The polymers which seemed to work best were those with about 2% of acid by weight in the polymeric chain.

Of the two acids used in the preparation of the co-polymers it was found that maleic acid containing polymers gave much better results than those containing acrylic acid.

CLAIMS

1. A process for de-inking paper pulp characterized by addition to the pulp of a surfactant having a character and composition generally similar to surfactants naturally present in the paper.

2. A process according to claim 1 characterized in that pulp to be de-inked is unbleached sulphite pulp and the added surfactant is of a type soluble in alkaline but relatively insoluble in acid solutions.

3. A process according to claim 2 characterized in that surfactant is an extract of the sulphite-insoluble hemicellulose fraction of wood pulp.

4. A process according to claim 3 characterized in that cellulose fraction is a mixture of polysaccharides and a minor proportion of side chain carboxyl groups.

5. A process according to claim 4 characterized in that the polysaccharides are based on xylose.

6. A process according to any one of the claims 3 to 5 characterized in that the process is carried out under alkaline conditions, and a level of calcium ions is present so as to form calcium salts of the hemicellulose.

7. A process according to claim 1 characterized in that the added surfactant is similar in structure to natural hemicellulose and contains a relatively high proportion of hydroxyl and a relatively low proportion of carboxyl groups in a linear polymeric structure.

8. A process according to claim 7 characterized in that the hemicellulose is made from vinyl acetate and acrylic acid by removing acetate residues by transesterification with methanol in the presence of sodium methoxide

9. A process according to claim 7 characterized in that the hemicellulose is made from vinyl acetate and maleic acid by removing acetate residues by transesterification with methanol in the presence of sodium methoxide.

10. A process for de-inking paper pulp according to claim 1 characterized in that the pulp is sulphite pulp and the added surfactant is a xylan polymer containing methylated glucuronic acid side-chains.

11. A method of manufacturing a synthetic co-polymer suitable for carrying out the process according to any one of the preceding claims, characterized in that the method used involves solution polymerisation.

12. A method of manufacturing a synthetic co-polymer suitable for carrying out the process according to claim 1, said method is characterized by the steps of dissolving a vinyl acetate monomer in toluene, adding hydroxy-propyl methacrylate and maleic or acrylic acid and AZBN as co-polymer initiator, heating the solution thus prepared, adding petroleum ether, adding methanol, followed by sodium methoxide and separating the co-polymer precipitated by the sodium methoxide.

13. A method according to claim 12 characterized by the modification of the initial addition of maleic or acrylic acid in place of subsequent addition thereof.

14. A method according to claim 12 or claim 13 characterized by the addition of dodecyl mercaptan, iso-propyl alcohol or other chain terminator.

15. A method according to claim 12, characterized in that reactants are 50 gm. vinyl acetate, 25 gm. of methyl acetate, 0.3 gm. AZBN, and during the first two hours of heating under reflux 25 gm. of methyl acetate, 0.15 gm. of maleic acid and 0.2 gm. AZBN are added.

16. A process for de-inking paper pulp substantially as hereinbefore described.

17. A method of manufacturing surfactants for us in the de-inking of paper pulp substantially as hereinbefore described in any one of the Examples.

18. Surfactant, when prepared by a method claimed in any one of claims 11 to 15 or claim 17.

19. Paper pulp de-inked by the by the process according to any one of the claims 1 to 9 or 16.

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 79/00202

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int. Cl.^{3}: D 21 C 5/02; C 08 B 37/14; C 08 F 8/12, C 08F 218/08// (C 08 F 218/08, C 08 F 220/06); (C 08 F 218/08, C 08 F 222/02); ./.

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
Int. Cl.^{3}	C 08 B 37/14; C 08 F 2/06; C 08 F 8/12; C 08 F 218/04 C 11 D 1/00; C 11 D 3/22; C 11 D 3/37; D 21 C 5/02 ./.

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
	GB, A, 1517262, published July 12, 1978; see page 1, line 82 to page 2, line 84; page 3, line 45 to page 4, line 83; Solvay	1,7-9,11, 16-19

	DE, A, 1904940, published August 6, 1970; see claims 1-3; page 2, last paragraph; page 3; page 6, paragraph 3; page 11, last paragraph; page 12, paragraph 1; Degussa	7-9,11,17, 18

	GB, A, 1385131, published February 26, 1975; see page 1, line 83 to page 2, line 68; examples B and C; ICI US	7,9,11,17, 18

	GB, A, 1284815, published August 9, 1972; see claims 1-3; page 2, lines 33-117; examples 1-3;	7,9,18

	US, A, 3284364, published November 8, 1966; see column 1, line 8 to column 2, line 62; examples 1-9; F.H. Siegele	7,8,17,18

	US, A, 3 061 551, published October 30, 1962;	2-6 ./.

* Special categories of cited documents: [15]

"A" document defining the general state of the art

"E" earlier document but published on or after the international filing date

"L" document cited for special reason other than those referred to in the other categories

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but on or after the priority date claimed

"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention

"X" document of particular relevance

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2] February 25, 1980	Date of Mailing of this International Search Report [2] March 7, 1980
International Searching Authority [1] European Patent Office	Signature of Authorized Officer [20] G.L.M. KRUYDENBERG

Form PCT/ISA/210 (second sheet) (October 1977)

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 79/00202

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

(C 08 F 218/08, C 08 F 220/06, C 08 F 220/20,
C 08 F 222/02)

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
Int. Cl.^{3}	D 21 C 9/08; D 21 H 3/20

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
	see column 1, lines 10-23 and 63-72; column 2, lines 48-72; column 3, lines 1-30; examples VIII and XI; M.W. Rutenberg et al.	
	US, A, 2801955, published August 6, 1957; see column 1, line 12 to column 2, line 33; M.W. Rutenberg et al.	6
	US, A, 2868778, published January 13, 1959; see column 2, line 20 to column 3, line 60; S.A. Watson et al.	6
	US, A, 3617431, published November 2, 1971; see column 1, line 6 to column 2, line 75; I.L.A. Croon et al.	1,4,5
	US, A, 3203918, published August 31, 1965; see column 1, line 11 to column 3, line 55; column 4, lines 59-64; examples I-III; A.I. Goldberg et al.	11-13,15
	GB, A, 1455741, published November 17, 1976;	11,12,17 ./.

* Special categories of cited documents: [15]

"A" document defining the general state of the art

"E" earlier document but published on or after the international filing date

"L" document cited for special reason other than those referred to in the other categories

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but on or after the priority date claimed

"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention

"X" document of particular relevance

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
International Searching Authority [1]	Signature of Authorized Officer [20]

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

	see page 1, line 79 to page 2, line 80; BASF	
	US, A, 3268491, published August 23, 1966; see column 1, lines 11-38; K.I. Hatton et al.	1,9,11
	US, A, 3816238, published June 11, 1974; see column 1, line 4 to column 2, line 62; column 3, lines 3-10; P.A. Mitchell	1,7,8

V.☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [10]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1.☐ Claim numbers ...., because they relate to subject matter [12] not required to be searched by this Authority, namely:

2.☐ Claim numbers ...., because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out [13], specifically:

VI.☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [11]

This International Searching Authority found multiple inventions in this international application as follows:

1.☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2.☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3.☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.