



Office de la Propriété
Intellectuelle
du Canada

Un organisme
d'Industrie Canada

Canadian
Intellectual Property
Office

An agency of
Industry Canada

CA 2076011 C 2001/10/02

(11)(21) **2 076 011**

(12) **BREVET CANADIEN
CANADIAN PATENT**

(13) **C**

(86) Date de dépôt PCT/PCT Filing Date: 1991/06/20
(87) Date publication PCT/PCT Publication Date: 1992/01/09
(45) Date de délivrance/Issue Date: 2001/10/02
(85) Entrée phase nationale/National Entry: 1992/08/07
(86) N° demande PCT/PCT Application No.: GB 91/00996
(87) N° publication PCT/PCT Publication No.: WO 92/00247
(30) Priorité/Priority: 1990/06/29 (546,435) US

(51) Cl.Int.⁵/Int.Cl.⁵ C02F 1/56
(72) Inventeurs/Inventors:
Fairchild, Hubert, Jr., US;
Payne, Geoffrey L., US
(73) Propriétaire/Owner:
CIBA SPECIALTY CHEMICALS WATER TREATMENTS
LIMITED, GB
(74) Agent: BORDEN LADNER GERVAIS LLP

(54) Titre : PURIFICATION DE LIQUEUR AQUEUSE
(54) Title: PURIFICATION OF AQUEOUS LIQUOR

(57) **Abrégé/Abstract:**

An aqueous suspension of coagulatable material is coagulated by adding polymeric coagulant to the suspension and then separating the resultant coagulated material from the liquor. The coagulatable material may be present in the aqueous suspension as a suspension of suspended solids or as colloidally dispersed solids. The suspension may be coal tailings or other aqueous (generally mineral) suspension. The polymeric material must be a low molecular weight, highly ionic, polymeric material. It is added to the aqueous suspension while in the form of polymeric particles having a size mainly above 30 µm and that will dissolve into the suspension and coagulate the coagulatable material. A counterionic, high molecular weight, flocculant is generally added subsequently in order to flocculate the coagulated material.





PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C02F 1/54, 1/52	A1	(11) International Publication Number: WO 92/00247 (43) International Publication Date: 9 January 1992 (09.01.92)
(21) International Application Number: PCT/GB91/00996 (22) International Filing Date: 20 June 1991 (20.06.91) (30) Priority data: 546,435 29 June 1990 (29.06.90) US (71) Applicant: ALLIED COLLOIDS LIMITED [GB/GB]; P.O. Box 38, Low Moor, Bradford, West Yorkshire BD12 0JZ (GB). (72) Inventors: PAYNE, Geoffrey, Laurence ; 120 Northgate Lane, Suffolk, VA 23434 (US). FAIRCHILD, Hubert, Jr. ; H.C. 60, Box 3370, Oil Springs, KY 41238 (US). (74) Agent: LAWRENCE, Peter, Robin, Broughton; Gill Jen- nings & Every, 53 to 64 Chancery Lane, London WC2A 1HN (GB).		(81) Designated States: AT, AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CA, CF (OAPI patent), CG (OAPI patent), CH, CH (European patent), CI (OAPI patent), CM (OAPI patent), CS, DE, DE (European patent), DK, DK (European patent), ES, ES (European patent), FI, FR (European patent), GA (OAPI patent), GB, GB (Eu- ropean patent), GN (OAPI patent), GR (European pa- tent), HU, IT (European patent), JP, KP, KR, LK, LU, LU (European patent), MC, MG, ML (OAPI patent), MR (OAPI patent), MW, NL, NL (European patent), NO, PL, RO, SD, SE, SE (European patent), SN (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent). Published <i>With international search report.</i>
(54) Title: PURIFICATION OF AQUEOUS LIQUOR (57) Abstract An aqueous suspension of coagulatable material is coagulated by adding polymeric coagulant to the suspension and then separating the resultant coagulated material from the liquor. The coagulatable material may be present in the aqueous suspension as a suspension of suspended solids or as colloiddally dispersed solids. The suspension may be coal tailings or other aqueous (generally mineral) suspension. The polymeric material must be a low molecular weight, highly ionic, polymeric material. It is added to the aqueous suspension while in the form of polymeric particles having a size mainly above 30 µm and that will dissolve into the suspension and coagulate the coagulatable material. A counterionic, high molecular weight, flocculant is generally added subsequently in order to flocculate the coagulated material.		

Purification of Aqueous Liquor

This invention relates to processes of coagulating aqueous suspensions of coagulatable material using water-soluble polymeric coagulants. The aqueous
5 suspensions can be true suspensions of suspended material or they can be liquors containing colloiddally dispersed material. The suspended or dispersed material is usually solid.

Aqueous suspensions are usually clarified by the
10 addition of one or more water-soluble organic polymers that are called coagulants or flocculants. These terms tend to be used rather inaccurately. In this specification, we use the term "flocculant" to denote a high molecular weight polymer that achieves its effect (i.e. flocculation)
15 primarily by a bridging mechanism, with the result that they are sometimes referred to as bridging flocculants. We use the term "coagulant" to indicate a lower molecular weight, highly ionic, material that achieves its effect (i.e. coagulation) primarily by adsorbing onto the
20 particles of the suspension and changing the surface charge on them, with little or no bridging effect between particles. As a result, the coagulants are sometimes referred to as charge neutralisation coagulants.

The coagulants have low molecular weight and because
25 of this, and their high ionic content, they have low solution viscosity and dissolve easily into water. Typically, the molecular weight of coagulants is never more than around 1.5 million and it is often below 1 million, and indeed when the polymer is anionic it is usually below
30 0.5 million. In terms of intrinsic viscosity, IV is usually below 3dl/g and generally below 2dl/g.

Throughout this specification, molecular weights are the values obtained by gel permeation chromatography and intrinsic viscosities are the values obtained using a
35 suspended level viscometer at 25°C in 1 molar sodium chloride aqueous solution buffered to pH 7.0.

SUBSTITUTE SHEET

Because of the low solution viscosity of these polymers, it is possible to provide aqueous concentrates that have a satisfactory combination of viscosity and polymer concentration. These concentrates are very easy
5 to use since they can be dosed direct into the suspension that is to be treated or can easily be diluted in-line with dilution water to form a dilute solution that can then be dosed into the suspension.

Many methods have been described in the literature for
10 making solid forms of water soluble polymers of various molecular weights. Solid forms do, of course, have the advantage that they do not necessitate the transport and packaging of large amounts of water and so can be more convenient, especially to the manufacturer, than aqueous
15 concentrates. However they have not been adopted widely and solid coagulants only constitute a very small proportion of the total polymeric coagulant market. For instance an important coagulant is polydiallyldimethyl ammonium chloride, and large amounts of this are supplied
20 worldwide. However only one grade is available in solid form, namely Percol 368 and Magnafloc 368, from Allied Colloids Inc. and Allied Colloids Limited respectively and this constitutes only a small proportion of the total sales of this polymer.

25 A solid grade coagulant must, of course, be in solution form before it can function as a coagulant and, heretofore, this has necessitated the user providing dissolution make-up equipment. The convenience and economy to the manufacturer of supplying a solid, without
30 the need to package and transport water, has therefore tended to be outweighed by the user preferring to obtain what was considered to be equivalent performance but without the inconvenience of having to provide make-up equipment.

35 An entirely different situation applies to flocculant polymers since these are always much higher molecular weight and many of them tend to dissolve only very slowly

into water. For instance flocculant polymers generally have molecular weights of at least 4 million and usually at least 5 million, and frequently above 10 million. Intrinsic viscosity is generally above 5dl/g and frequently
5 above 10dl/g, especially with the anionic and non-ionic polymers.

Because of the high molecular weights, flocculant polymers have very high solution viscosities and so it is not possible to supply handlable concentrates having
10 adequate polymer concentrations. Accordingly, the flocculants generally have to be supplied as powders or as dispersions in oil. The polymer then has to be dissolved into water. The rate of dissolution depends upon ionic charge and molecular weight. Some dissolution can occur
15 with some polymers within a few minutes, but many of the polymers take at least an hour to go to full solution. Such polymers include, for instance, many of the polyacrylamides. Since the flocculant polymers cannot exert their bridging effect until they are in proper
20 solution, it is therefore conventional for the user to install sufficient make-up apparatus to ensure that the flocculant can be truly dissolved before it is dosed into the suspension that is to be treated. Such make-up apparatus generally has to involve a storage vessel that
25 can hold the flocculant for at least an hour while it goes into true solution.

Although this is true of normal flocculation processes, a few exceptions to this general rule have been proposed in the literature.

30 For instance in JP-A-48084776 and JP-A-49049802 high molecular weight flocculant is added as powder direct into a sludge that is being transported or pumped into a pit. In each instance the flocculant is partially hydrolysed polyacrylamide of molecular weight 5 million or more, and
35 so presumably is not highly anionic (depending on the degree of hydrolysis). Also, it is known to add flocculant powder to a slurry of mine tailings that is

SUBSTITUTE SHEET

being pumped down through a mine to form a backfill. In all these processes, the flocculant powder can be in contact with the slurry for a considerable time before it needs to complete its flocculation effect, and so there is
5 time for the powder to dissolve. Similarly, in JP-A-60282787 a mixture of high molecular weight powdered flocculants is added to an emulsion but again the separation process appears to be sufficiently slow to permit dissolution.

10 The main difficulty with such methods is that high molecular weight flocculants only dissolve slowly. It has been proposed to treat the polymer particles in various ways, presumably with the intention of accelerating their rate of dissolution. Disclosures of such processes are in,
15 for instance, JP-A-50003974, JP-A-49121309, JP-A-58070807 and JP-A-58089915 and US 4089831. It is also known to dissolve high molecular weight polymeric flocculant from within bags and shaped articles that are immersed for prolonged periods in a flowing suspension, for instance as
20 described in JP-A-53091072 and JP-A-56115605 and EP-A-255283.

All these methods tend to utilise polymer at a rather uncontrollable rate and so may suffer from underdosing or overdosing.

25 Although it is normally required for the polymer to be in true solution to function effectively there have been some disclosures (e.g., U.S. 3,235,490 and 3,021,269) where apparently cross linked and potentially insoluble polymers were homogenised before use as flocculants so as to permit
30 them to form what appears to be a true solution of relatively low molecular weight polymer. Other disclosures of increasing the suitability of polymers by shearing are in U.S. 4,705,640 and 4,759,856.

Whereas true solubility is normally required before
35 contact with the aqueous suspension, in U.S. 4,720,346 the polymer is a high molecular weight synthetic polymeric flocculant and performs its flocculating function on the

SUBSTITUTE SHEET

suspended solids while the polymer is still in the form of polymeric particles having a size of below $10\mu\text{m}$. These particles can, if left long enough, be truly soluble in water but preferably the polymer is cross linked so that
5 they cannot dissolve fully into water.

The very small particle size, of below $10\mu\text{m}$, is essential. Normally it is provided by introducing the polymer particles as a dispersion that has been made by reverse phase polymerisation but in EP-A-326382 it is
10 provided by introducing the polymer in the form of friable aggregates that have been made by bonding the substantially dry polymer particles having a size of below $10\mu\text{m}$ with an aqueous liquid and drying the aggregates, whereby the aggregates disintegrate upon addition to water to release
15 the individual polymer particles.

In all coagulation and flocculation processes, there is always the desire to achieve better performance, leading to better clarity or reduced consumption of polymer or both, and/or to achieve simpler techniques of operation.

20 It is accordingly an object of the invention to provide improved processes for the separation of dispersed or suspended material from aqueous dispersions and suspensions. It is a further object to provide such processes that use polymer in the form of a powder but
25 which avoids the need for normal solids make-up apparatus and eliminates the need for normal concentrate handling equipment such as pumps and in-line dilution equipment. It is a further object of the invention to provide improved separation of solids from the suspension when treated by
30 the treatment polymer.

In particular, it is an object of the invention to provide an improved way of supplying and utilising ionic coagulant polymer having a sufficiently low molecular weight that it can normally be supplied as a aqueous
35 concentrate but which, for convenience, is supplied as a powder. A further object is to obtain improved performance.

SUBSTITUTE SHEET

The invention provides a process of coagulating an aqueous suspension of coagulatable material by using a water-soluble, low molecular weight, ionic polymeric coagulant. This results in coagulation of the
5 coagulatable material, and the coagulated material is then separated from the suspension.

In particular, the process comprises providing a particulate, water soluble, ionic, polymeric coagulant that has intrinsic viscosity of 0.2 to 3dl/g and that is in the
10 form of solid particles that have a size of at least 90% by weight above $30\mu\text{m}$, mixing the said solid particles into the suspension and thereby dissolving the particles in the suspension and coagulating the suspension, and subjecting the coagulated suspension to a separation process and
15 thereby separating said coagulatable material from said liquor.

In the preferred process a low molecular weight ionic coagulant polymer, preferably of diallyl dimethyl ammonium chloride, is added as solid particles to a suspension that
20 is to be coagulated and dissolves rapidly in the suspension and coagulates it, and the coagulated material is separated from the suspension. Generally this separation is facilitated by adding a flocculant to the coagulated suspension, for instance by adding a conventional
25 counterionic high molecular weight flocculant solution to the suspension.

We have surprisingly found that the addition of solid, low molecular weight, ionic coagulant to the suspension generally gives a significant, and often very highly
30 significant, improvement in coagulation performance relative to when the equivalent polymer is added to the suspension as a solution in conventional manner.

By the invention, the performance properties are always as good as those obtained using a polymer solution
35 and, as indicated, they are usually very much better, and yet the invention has the further advantage that it eliminates the need for equipment for handling aqueous

concentrates (e.g., pumps and in-line dilution equipment) and it avoids the equipment traditionally associated with solid grade polymers, namely the make-up equipment that is traditionally installed to allow the solid grade polymer to
5 be put into the form of a solution prior to dosage into the suspension.

We are unclear as to why it is possible, by this technique, to obtain better results than are obtainable using a preformed solution of the same polymer, but it may
10 be associated in some way with the polymer being released continuously over a useful period into the suspension. Thus it seems that as polymer molecules dissolve from the solid polymer particles, these molecules are absorbed substantially immediately on to the coagulatable material
15 to form the desired ionic surface characteristics on the particles of coagulatable material. If agitation or other effects cause a deficiency of polymer (and therefore of ionic charge) on part of the surfaces of suspension particles, this deficiency is probably made up by fresh
20 polymer that is still dissolving from the polymer particles. This is in contrast to conventional processes where all the polymer is made available instantaneously as a solution. Once that polymer has been adsorbed onto the particles there will probably be a much lower tendency for
25 fresh polymer to be available to adsorb onto any surfaces where there is a deficiency of polymer, for instance as a result of breakdown of the coagulated particles.

However, irrespective of the reason or the mechanism, the process definitely has the advantage that it is
30 possible to obtain greatly improved performance at the same time as using a solid material by a simplified process and apparatus and without a make-up or dilution stage.

The term "coagulatable material" is used herein to embrace both materials that are already present as
35 suspended solids and materials that are present as a colloidal dispersion. Thus it embraces particulate solids such as pigment, clay, coal and sewage solids, and it also

embraces colloiddally dispersed materials such as colouring matter in water and humates. The process of the invention can bring more of this colloiddally dispersed material out of colloidal solution as a particulate solid than when the
5 same polymer is added as a solution.

Flocculation processes involving bridging flocculants can be relatively slow and indeed bridging may occur during, for instance, sedimentation after addition of a flocculant. However coagulation processes depend
10 primarily upon charge effects and coagulation processes therefore tend to be very fast. For instance, coagulation often precedes the addition of a bridging flocculant, and this is generally added very soon after the coagulant.

In the invention, the polymeric coagulant starts
15 dissolving immediately upon contact with the suspension, because the coagulant is water soluble. Accordingly it immediately makes coagulant polymer molecules available for coagulation. It is preferred that the polymer particles do go into substantially complete solution in less than
20 about five minutes and preferably much quicker, generally within about one minute and preferably within about thirty seconds, often within about fifteen seconds.

Whether or not a polymer particle has dissolved can be determined by filtration in that a screen that retains a
25 dry or gelled polymer particle will not retain a solution of the polymer particle. A convenient way of testing the solubility therefore is to select a screen that retains a known proportion, for instance substantially all, of the polymer particles when dry and then to filter the aqueous
30 suspension into which the polymer particles have been mixed and observe the proportion of polymer particles retained on the screen. The retained proportion at the end of the mixing period (i.e., when they should be substantially fully dissolved) must be very much less than the retained
35 proportion of dry polymer particles, for instance having a dry weight below a quarter and preferably below one tenth of the weight of the retained dry particles.

SUBSTITUTE SHEET

Generally the polymer particles are substantially individual particles but if they are aggregates that break down into smaller particles before dissolution (for instance as in EP 326382) then the size of screen that should be used for testing whether or not dissolution has occurred should be the size that retains the individual component particles within each aggregate.

The optimum duration for dissolution will depend upon the particular suspension and process that is being coagulated. If the rate of dissolution is too slow, some of the polymer may remain undissolved during the period when a coagulation effect is required, for instance during passage in a flow line to a flocculation stage, and so may involve the use of more polymer than would be required if it dissolved faster. Preferably the polymer is substantially fully dissolved before the suspension reaches the next treatment stage, and in particular before it reaches the next point of addition of treatment chemical, for instance bridging flocculant.

Although the polymer particles (or the component particles within aggregates that disintegrate into particles in the suspension) can have a size as small as $30\mu\text{m}$ it is generally preferred for the average size to be at least $100\mu\text{m}$ and generally at least $200\mu\text{m}$. If the polymer particles have an average size that is too large then this can be undesirable, for instance because it can reduce the time taken to achieve dissolution. Thus although it can be above 1mm , preferably it is below 1mm and usually below $800\mu\text{m}$. It is generally preferred for the polymer particles to have a size of at least 90% by weight in the range $100\mu\text{m}$ to $1,000\mu\text{m}$, often in the range $200\mu\text{m}$ to $800\mu\text{m}$. Although it is normally preferred for polymers to have a reasonably narrow range of particle sizes, in the invention it can be advantageous to have a relatively wide spread of particle sizes so as to spread the time over which polymer dissolves.

SUBSTITUTE SHEET

The ionic coagulant polymers with which this invention is concerned are the materials that have, heretofore, usually been supplied as aqueous solutions because of their low solution viscosities, and therefore the particles will inevitably tend to start dissolving very quickly, and generally will be substantially fully dissolved within about a minute, often within about half a minute. These low solution viscosity and high dissolution rates are associated with the charge density and the molecular weight (intrinsic viscosity) of the polymer. If the molecular weight is too high then the polymer will not be an ionic coagulant but will instead tend to be a bridging flocculant and, in any event, will have a solution viscosity such that it is not commercially convenient to supply it as an aqueous concentrate. The optimum intrinsic viscosity depends upon the ionic charge and the particular polymer. When the polymer is a cationic polymer, intrinsic viscosity is generally at least about 0.2, preferably in the range of about 0.5 to 3, most preferably around 0.8 to 2.4dl/g. Expressed in terms of molecular weight, it is generally preferred for the molecular weight to be below 2 million, most preferably below 1.5 and, preferably, below 1 million, although it should generally be above 100,000 and preferably above 500,000.

When the polymer is anionic, lower molecular weights are usually desirable, and in particular the anionic polymer should have a molecular weight below 1,000,000, most usually below 500,000. It must not be too low as otherwise it will act as a dispersant rather than a coagulant and so normally the molecular weight is above 50,000, often above 100,000. Expressed in terms of intrinsic viscosity, this should normally be at least 0.2dl/g and is preferably not more than about 2dl/g. Preferably intrinsic viscosity is in the range about 0.5 to 2dl/g, most preferably about 0.8 to 1.5dl/g.

The polymer can be a low molecular weight, rapidly dissolving, highly ionic, naturally occurring polymer but

generally it is a synthetic polymer formed by polymerisation of a water soluble ethylenically unsaturated monomer or blend of monomers and has a high charge density.

Accordingly it is preferred for at least 50%, and
5 generally at least 80%, of the monomers from which it is formed to have an ionic charge. Although the polymer can be amphoteric, preferably all the ionic monomers have the same charge. Although polymers in which 100% of the
10 monomers are ionic are preferred, if non-ionic monomer is present its amount is generally below 50%, and preferably below 20% by weight. Any of the non-ionic, ethylenically unsaturated, water soluble monomers that are conventionally present in polymeric ionic coagulants can be used, but acrylamide is preferred. It is generally best for the
15 polymer to be a homopolymer of ionic monomer.

Preferred anionic monomers are ethylenically unsaturated carboxylic or sulphonic acids (including their water soluble alkali metal or other salts). Examples are
20 2-acrylamido-2-methyl propane sulphonic acid, methacrylic acid and, especially, acrylic acid. Thus a suitable anionic polymer is a homopolymer of sodium acrylate.

Preferred cationic monomers are dialkylaminoalkyl (meth) -acrylates and -acrylamides, generally as acid addition or quaternary ammonium salts, and diallyl dialkyl
25 ammonium halides. The preferred acrylates and methacrylates are preferably di-C₁₋₄ alkylaminoethyl (meth) acrylates and the preferred acrylamides are di-C₁₋₄ alkylaminopropyl (meth) acrylamides, in particular dimethylaminoethyl (meth) acrylate and dimethylaminopropyl
30 (meth) acrylamide (with the respective methacrylate and methacrylamide compounds being particularly preferred) as acid addition and quaternary ammonium salts. For most purposes the most suitable cationic monomer is diallyl dimethyl ammonium chloride. Generally a single cationic
35 monomer is used, but if desired a copolymer may be formed, for instance from diallyl dimethyl ammonium chloride and

dimethylaminopropyl methacrylamide salt, generally with the latter in a minor proportion.

Instead of forming the polymer by addition polymerisation of ethylenically unsaturated monomers, any other known ionic coagulant polymers can be used. For instance suitable polymers are polyethylene imine and polyamines, e.g., as made by condensation of epichlorhydrin with an amine. Other polymers include aminomethylolated polyacrylamide (free base or quaternary or acid salt), poly (2-hydroxypropyl-1-N-methylammonium chloride), poly (2-hydroxy-propyl-1, 1-N-dimethylammonium chloride, and poly (2-vinylimidazolinum bisulphate.

Particularly preferred polymers for use in the invention are polymers of diallyl dimethyl ammonium chloride, generally as homopolymers but optionally with up to 20% of other monomer, generally acrylamide, having IV of about 0.6 to 3, most preferably around 0.8 to 2.5dl/g. Preferably the polymer is in the form of beads.

The particles of polymer are preferably substantially bead shaped, for instance as made by reverse phase suspension polymerisation. Reverse phase suspension polymerisation typically comprises dispersing beads of aqueous monomer in a water immiscible liquid, generally in the presence of amphiphilic polymeric stabiliser, polymerisation within the beads, drying by azeotropic distillation and then separation of the beads from the liquid, often followed by further drying. Suitable methods and materials are well known and are described in, for instance, US 2,982,749, 4,506,062 and 4,528,321.

Other solid particulate forms can be used. For instance a solution of the polymer can be drum dried or otherwise dried as a film which can then be converted into flakes. If the polymer itself has characteristics such that it is difficult to provide it in the form of solid particles that can be handled without, for instance, caking, then the particles can be formed of a mixture of a carrier (that promotes formation of particles) and the

polymer. For instance the polymer can be distributed throughout beads of a matrix material that will liberate the polymer rapidly upon contact with water, for instance as a result of disintegration of the matrix in water. A
5 suitable matrix material is a carbohydrate, for instance starch, or an inorganic carrier material. The blend can be made as in, for instance, EP-A-188489. Preferably however the polymer particles consist solely of the desired polymer.

10 Suitable polymers are available in bead form from Allied Colloids Inc. and Allied Colloids Limited under the trade names Magnafloc 368, Percol 368 (cationic polydiallyldimethyl ammonium chloride) and Versicol S11 (anionic polyacrylic acid).

15 The mixing of the particulate polymeric coagulant into the suspension is normally accompanied by some degree of agitation of the suspension, although with highly soluble particles adequate mixing may be achieved merely by adding the particles to the suspension. Generally however some
20 degree of turbulence should be applied to the suspension to promote dissolution of the particles. The turbulence that inevitably arises during flow of a stream that is being coagulated in conventional manner can be sufficient and excessive shear (eg as provided in a homogeniser) is
25 undesirable. Accordingly the preferred mixing consists essentially of the flow along duct means leading to the separation stage, although some initial mixing may be applied to promote uniform distribution of the polymer particles as they are scattered, flowed or injected into
30 the flowing suspension.

The process may be carried out batchwise, but generally the particles are added to a flowing stream of the suspension and the suspension is caused to flow turbulently along duct means from the position at which the
35 particles are added to the position at which the separation process is initiated. For instance this flow can be along a simple duct (optionally as a launder provided with

baffles to create extra turbulence) or it can be along a series of ducts, for instance including some substantially downwardly extending ducts so as to promote extra turbulence.

5 In conventional coagulation and flocculation processes, the respective polymers are added as fully dissolved aqueous solutions and it is well known that it is then undesirable to continue applying shear (i.e., to continue turbulence) for too long since this tends to
10 result in resuspension of the originally suspended particles and reduction in performance. However in the invention excess shear is not so undesirable, and indeed can be positively advantageous, since fresh polymer molecules can continuously be dissolved from the polymer
15 particles and so even if the distribution of polymer on the particles of the original suspension is damaged fresh polymer molecules are available to recoagulate the surfaces of the suspension particles. Nevertheless, it is generally desirable that the entire coagulation process,
20 and in particular the mixing or application of shear that occurs during the process, should be relatively short and preferably mixing does not continue for significant periods after the polymer has dissolved.

 In preferred processes, the total time that elapses
25 between initially adding the polymer particles and introducing the coagulated suspension to the separation process apparatus (.e.g, a sedimentation vessel) is not more than about one minute, preferably not more than about thirty seconds, and most preferably not more than about
30 fifteen seconds, and during this time the polymer particles should have been substantially fully dissolved.

 As is known, there are some instances where a coagulant polymer by itself (conventionally added as a solution) will give adequate coagulation and separation,
35 without any subsequent chemical treatment. Accordingly, this is also possible in the invention.

SUBSTITUTE SHEET

However, it is more normal to follow the addition of a coagulant solution with the addition of a flocculant solution, and in the invention it is usually preferred to incorporate a polymeric flocculant into the suspension after the coagulant polymer has dissolved and coagulated the suspension. The incorporation of the flocculant may be by conventional means, such as the addition of flocculant solution followed by brief (e.g., up to 15 seconds and often less than 5 seconds) agitation to achieve thorough mixing.

When flocculant is used, it is usually counterionic to the coagulant polymer that is added in particulate form. The coagulant polymer is preferably cationic, and so the flocculant is preferably anionic. However in some instances anionic coagulant followed by anionic flocculant can be useful, e.g., on some coal washery slurries. A surprising advantage of the invention is that the amount of flocculant that is required to achieve any particular level of clarification is generally less, when the coagulant polymer is added in particulate form, than when the coagulant polymer is added as a solution. For instance the amount of counterionic flocculant may be one fifth to three quarters, typically around half, of the amount normally required.

The flocculant may be any of the conventional bridging flocculants, and thus should have a sufficiently high molecular weight to give a bridging, as opposed to a coagulating, mechanism. Typically therefore the molecular weight is at least 5,000,000 and/or intrinsic viscosity is preferably at least 6dl/g. The polymeric flocculant can be a natural or modified natural polymer but is generally a synthetic polymer formed from the monomers listed above. Since the coagulant is preferably cationic, the flocculant is preferably anionic, often sodium polyacrylate or a copolymer with acrylamide.

When the suspended material is solid (i.e., suspended or colloidally dispersed solids), the separation process

preferably comprises a sedimentation process. It can consist solely of sedimentation but generally it involves a further dewatering step. Any such further dewatering step is generally conducted on the sediment obtained by the sedimentation. Such further processes include centrifugation and filtration, e.g., on a filter press or belt press.

One particularly preferred process of the invention involves applying the process to tailings from a coal washer or from an iron ore concentrator. Thus coal or iron ore is washed and the desired product (coal or iron ore) is separated by sedimentation or other appropriate separation technique to leave a liquor, termed tailings, that is a suspension of the waste products. These waste products often comprise clay. Most of the solids may be suspended solids but some can be colloiddally dispersed, as colourants. Conventional processes involve adding a solution of coagulant polymer to the tailings as they flow along a duct towards a sedimentation tank, with flocculant solution generally being added immediately before the sedimentation tank. The liquor resulting from the sedimentation generally still contains some suspended solids and can be coloured.

By the invention, it is possible to obtain much better separation of solids, and in particular to remove not only substantially all the suspended solids but also most of the colourant. Thus the process of the invention can result in a very clear, less coloured, liquor than is obtainable by conventional techniques, and yet avoids the need for a make-up unit or for the pumps or in-line dilution apparatus normally associated with the use of aqueous concentrates.

The preferred polymer for use in this technique is a homopolymer of diallyl dimethyl ammonium chloride (or occasionally a copolymer with up to 20% acrylamide) having intrinsic viscosity 0.5 to 3 (preferably 0.8 to 2.5) dl/g and that preferably fully dissolves within about one minute, preferably within about thirty seconds and most

preferably within about fifteen seconds. The polymer is preferably added in the form of beads which typically mainly have a size in the range 200 to 1000 μ m. A solution of flocculant (e.g., sodium polyacrylate molecular weight
5 above 5 million) can be added immediately prior to the sedimentation tank. The total time between adding the particles and introducing the suspension into the sedimentation tank is generally less than one minute, preferably less than about thirty seconds and most
10 preferably is less than about fifteen seconds.

Although the polymers of diallyl dimethyl ammonium chloride are particularly suitable for this process, other low molecular weight cationic polymers can be used, for instance polymers of cationic (meth) acrylates or cationic
15 (meth) acrylamides, as discussed above.

Although the process is of particular value when applied to suspensions that are mineral washery tailings, such as iron ore and coal washery tailings, it has surprisingly been found that it is also of value on a range
20 of other industrial waste waters and other suspensions.

One important aspect of the invention arises when the aqueous suspension is a china clay effluent, for instance in the winning of such clays.

Another important aspect of the invention is in the
25 treatment of waste water from the feldspar and alumina industries. In particular, red mud washery liquors contaminated with colloidal humate can be decolourised by the addition of the chosen polymer in particulate form, instead of adding it in the conventional solution form as
30 proposed in U.S. 4,578,255.

In addition to being of use in the treatment of mineral suspensions, the invention is also of value in the treatment of organic suspensions and in the production of potable water. Less preferably, it can be used in cracking
35 of oil-in-water emulsions.

Another important aspect of the invention is when the suspension is a cellulosic suspension, for instance a white

SUBSTITUTE SHEET

water effluent from a paper mill or some other suspension associated with paper production and that needs to have solids removed and to be decolourised, for instance by the removal of fibres, resinous materials and lignins.

5 Another important aspect of the invention includes the treatment of suspensions comprising sewage solids, for instance sewage sludge.

 Another important aspect of the invention involves the removal of colouring matter and optionally suspended solids
10 from potable water, typically prior to sedimentation or filtration through a sand bed.

 Another important type of suspension is a coloured effluent from the textile industry, where the process is designed to decolourise the effluent.

15 In a further aspect of the invention, the coagulatable material is, at all relevant times, a liquid and thus is not suspended solids nor colloiddally dispersed solids. Thus the particulate coagulant may be added to an oil-in-water emulsion as a coagulant for cracking the
20 emulsion.

 The solids content of the suspension is generally below 10%, typically 0.02% to 8%, but another important aspect of the invention involves applying the process to suspensions having a higher solids content, typically 10 to
25 30%, for instance suspensions obtained by sedimentation in a previous separation process. Thus another process comprises dewatering a suspension (often after the addition of particulate coagulant as proposed in the invention) and then adding particulate polymer to the dewatered product
30 and subjecting it to further dewatering after the polymer has dissolved, in accordance with the invention.

 The optimum dosage of particulate coagulant polymer can be selected by routine experiments and is generally within or below conventional amounts of dissolved coagulant
35 polymer. For instance it is often 0.1 to 20, frequently 0.5 to 5 mg/l suspension.

 The following are examples of the invention.

SUBSTITUTE SHEET

Example 1

A homopolymer is formed from diallyl dimethyl ammonium chloride by reverse phase bead polymerisation by the general technique shown in U.S. 4,506,062. The beads have
5 a particle size of 90% by weight between 200 and 800 μ m and they have intrinsic viscosity of 1.4dl/g. Suitable beads are available from Allied Colloids Inc. under the trade name Percol 368.

Coal washings are subjected to froth flotation and the
10 tailings from the flotation cells drop around 30 metres from the cells down a duct to the ground and to a pump by which they are pumped about 100 metres vertically upwards to a feed launder leading to a feed well at the inlet to a sedimentation (or thickener) tank. A solution of anionic
15 polymeric flocculant (copolymer of 60% acrylamide 40% sodium acrylate, IV about 16 dl/g) is added at the feed well, so as to promote settling in the tank.

The tailings have pH 7.4, around 7% solids material of which around 75% is below 100 mesh and is mainly clay.

20 In one process the cationic polymer beads are screw fed into the tailings from the flotation cells as they leave the cells.

In another process an aqueous solution of a similar polymer is added into the feed launder to the sedimentation
25 tank.

It is found that addition of about 80g/min (dry weight) of the solution polymer gives clarified water containing 80 to 90NTU, whereas dosage of only 36g/m of the polymer beads gives clarified water of 60 to 70NTU and the
30 filtration of the sediment is performed more easily.

Example 2

The polymer of example 1 is fed into a stream of coal tailings discharging from a primary settling pond to a secondary settling pond. Flow is by gravity down a pipe
35 with a passage time of less than thirty seconds. The suspended solids of the overflow from the secondary settling pond is determined. With polymer dosages ranging

from 0.0025 to 0.0125 g/l, the suspended solids range from around 0.18% to 0.16% respectively.

When the same polymer is added as a 1% solution at polymer dosages of 0.0125 to 0.024g/l, the suspended solids range from 0.3% to 0.25% respectively. This again demonstrates the dramatic reduction in suspended solids obtainable by the use of the solid form of polymer in contrast to the solution form.

Example 3

In this example, the polymer is similar to example 1 except that it has higher molecular weight, intrinsic viscosity about 2dl/g.

12.5 litres of an 8% aqueous dispersion that is an iron ore tailings is agitated in a large bucket and 0.0027 grams polymer is added, with agitation continuing for 15, 30 and 60 seconds. Samples are taken after each period of agitation and the settling rate in inches (2.54cm) per minute is recorded. The highest value is desirable. A clarity wedge value is recorded after 10 minute settling, and again the highest result is desirable. The results are shown in the following table.

Mixing time	Dry Polymer		Solution Polymer	
	Settling Rate	Clarity Wedge	Settling Rate	Clarity Wedge
15 seconds	1.0	21	0.9	14
30 seconds	1.0	19	0.88	13
60 seconds	0.95	16	0.85	13

These results clearly demonstrate that the best results are obtained with the dry polymer, and that the results are better at 15 seconds mixing than at 60 seconds mixing.

Example 4

A slurry of 1% kaolin in water containing 1g/l sodium chloride is prepared. 1 litre of the slurry is placed in

a cylinder provided with a perforated steel plunger, depression of which causes mixing of the slurry. The test polymer is added, at dosages ranging from 1 to 5 mg/l and the slurry is subjected to 3, 6 or 9 plunges of the plunger.

The process is repeated using polymers of diallyl dimethyl ammonium chloride having, respectively, intrinsic viscosity 0.4, 0.9 and 2.0 dl/g. The settlement rate and clarity is recorded.

In every instance, the settlement rate is better, at a given number of plunges, for the solid polymer than the solution polymer and decreases with an increase in the number of plunges. In every instance the settlement rate of the polymer having IV 2 is better than the settlement rate for the polymer having IV 0.9 which, in turn, is better than the settlement rate for the polymer having IV 0.4dl/g.

Similarly, the compaction deteriorates (increases) with an increase in the number of plunges and with decreasing IV. In general, the compaction is always better with the solid polymer than with the corresponding solution polymer.

As regards clarity, there is little difference between the results obtained with the solid and solution polymers having IV 0.4 but the solid form of the other two polymers is always better than the solution form, with best results being obtained with the polymer having IV 2 and about 6 plunges.

The settlement rate and clarity each tend to improve as the dosage increases from 1 to 5 mg/l, except that with the polymer of IV 0.9dl/g the best settlement rate is achieved at a dosage of about 2.5 mg/l.

Example 5

A slurry is prepared of 1% china clay, 150mg/l sodium humate and 200g/l sodium hydroxide. 500ml samples of this slurry are stirred at 150rpm and dosed with various amounts of polymeric coagulant, either as solid or as aqueous

solution. Stirring is continued for 11 minutes and 2mg/l sodium polyacrylate (molecular weight above 5 million) is added and stirred in for the last minute.

5 A sample of supernatant is removed and the humate concentration in parts per million calculated from its UV absorbents. At 30 and 90 mg/l polydiallyl dimethyl ammonium chloride (IV 0.9dl/g) the humate concentrations are substantially the same both when introduced as solid and as liquid, but at 60mg/l dosage the humate
10 concentration is much lower (better) using the solid than the solution polymer (36ppm compared to 44ppm).

Example 6

A slurry is made up as in Example 4 and then tested as in Example 4 using, as the coagulant polymer, powdered (or
15 solution) sodium polyacrylate having molecular weight about 250,000. Turbidity and settlement rates are recorded. In every instance, the solid gives better settlement rate than the solution at 3 and 6 plunges, and although the trend continues to be true at higher numbers of plunges
20 (i.e., continued turbulence, it is less distinct). For instance the solid grade polymer at 1mg/l gives settlement rates of 7.6, 5.7 and 4.5cm/min at 3, 6 and 9 plunges respectively, whereas the corresponding values when the polymer is added as a solution are 4.7, 4.3 and 4.0cm/min.
25 There is no significant difference in turbidity obtained using solid or solution polymers in this example.

CLAIMS

1. A process of separating coagulatable material from an aqueous suspension of the coagulatable material, the process comprising:
- 5 providing a particulate, water soluble, ionic, polymeric coagulant that has intrinsic viscosity of 0.2 to 3dl/g and that is in the form of solid particles that have a size of at least 90% by weight above 30 μ m,
- 10 mixing the said solid polymer particles into the suspension and thereby dissolving the polymer particles in the suspension and coagulating the suspension, and
- subjecting the said coagulated suspension to a separation process and thereby separating said coagulatable material from said suspension.
- 15 2. A process according to claim 1 in which counterionic organic polymeric flocculant solution is added to the coagulated suspension to promote flocculation of the coagulated suspension before or during the said separation process.
- 20 3. A process according to claim 1 in which the said mixing comprises flowing the suspension along duct means for a period of not more than about 5 minutes from a position at which the particulate coagulant is added to the suspension to a position at which the said separation
- 25 process is initiated, and the coagulant particles substantially fully dissolve before the suspension reaches the said position at which the said separation process is initiated.
- 30 4. A process according to claim 1 in which the coagulatable material is a solid particulate material, the solubility of the coagulant polymer particles is such that they will substantially fully dissolve in less than about one minute, the mixing comprises flowing the suspension turbulently along duct means within a period of not more
- 35 than about one minute from a position at which the coagulant particles are added to the suspension to a position at which a solution of an organic polymeric

flocculant is added to promote flocculation of the suspension, and the suspension is substantially immediately subjected to the said separation process.

5. A process according to claim 1 in which the coagulant polymer particles have a size of at least 90% by weight between 100 μ m and 1000 μ m and are formed of monomers of which at least 50% by weight are ionic, the coagulant polymer particles have a solubility such that they will substantially fully dissolve into the suspension in less than about a minute and the said coagulated suspension is subjected to the start of the said separation process within about a minute of the start of the said mixing of the coagulant particles into the suspension, and the coagulatable material is selected from suspended solids and colloiddally dispersed solids.

6. A process according to claim 1 in which the mixing consists essentially of flowing the suspension turbulently along duct means, the suspended material is solid and the separation process comprises a sedimentation process and the coagulant polymer is cationic.

7. A process according to claim 4 in which the mixing consists essentially of flowing the suspension turbulently along duct means, the suspended material is solid and the separation process comprises a sedimentation process and the coagulant polymer is cationic.

8. A process according to claim 1 in which the coagulant polymer is selected from (a) cationic polymer that have intrinsic viscosity of from about 0.2 to 3dl/g and that are formed from ethylenically unsaturated monomers of which at least 50% by weight are cationic, and (b) anionic polymers that have intrinsic viscosity of from about 0.2 to 2dl/g and that are formed from ethylenically unsaturated monomers of which at least 50% by weight are anionic.

9. A process according to claim 1 or in which the polymer has intrinsic viscosity of from about 0.5 and 2.4dl/g and is selected from (a) polymers of 0 to 50% non-ionic ethylenically unsaturated monomer and 50 to 100% ionic

monomer selected from diallyl dialkyl ammonium halides, dialkylaminoalkyl (meth) acrylates acid addition and quaternary ammonium salts, and dialkylaminoalkyl (meth) acrylamides acid addition and quaternary ammonium salts,
5 (b) polyethylene imines and (c) polyamines.

10. A process according to claim 1 in which the polymer is selected from polymers of 0 to 20% acrylamide and 80 to 100% ionic monomer selected from diallyl dimethyl ammonium chloride, di-C₁₋₄ alkylaminopropyl (meth) acrylamide acid
10 addition and quaternary ammonium salts and di-C₁₋₄ alkylaminoethyl (meth) acrylate acid addition and quaternary ammonium salts.

11. A process according to claim 1 in which the polymer is a substantial homopolymer of diallyl dimethyl ammonium
15 chloride and has intrinsic viscosity of about 0.6 to 3dl/g.

12. A process according to claim 1 in which the aqueous suspension is selected from mineral washery tailings, industrial waste water, china clay suspensions, sewage suspensions, cellulosic suspensions, coloured potable
20 water, red mud washery liquor, and liquor containing humate.

13. A process according to claim 1 in which the aqueous suspension is selected from mineral washery tailings, industrial waste water, china clay suspensions, sewage
25 suspensions, cellulosic suspensions, coloured potable water, red mud washery liquor, and liquor containing humate and in which the coagulant polymer has intrinsic viscosity 0.5 to 3dl/g and is a polymer of 0 to 20% acrylamide and 80 to 100% ionic monomer selected from diallyl dimethyl
30 ammonium chloride, di-C₁₋₄ alkylaminopropyl (meth) acrylamide acid addition and quaternary ammonium salts and di-C₁₋₄ alkylaminoethyl (meth) acrylate acid addition and quaternary ammonium salts.

14. A process according to claim 4 in which the aqueous
35 suspension is selected from mineral washery tailings, industrial waste water, china clay suspensions, sewage suspensions, cellulosic suspensions, coloured potable

water, red mud washery liquor, and liquor containing humate and in which the coagulant polymer has intrinsic viscosity 0.5 to 3dl/g and is a polymer of 0 to 20% acrylamide and 80 to 100% ionic monomer selected from diallyl dimethyl ammonium chloride, di-C₁₋₄ alkylaminopropyl (meth) acrylamide acid addition and quaternary ammonium salts and di-C₁₋₄ alkylaminoethyl (meth) acrylate acid addition and quaternary ammonium salts.

15. A process according to claim 1 in which the suspension is selected from coal and iron ore washery tailings, the particulate polymeric coagulant has intrinsic viscosity 0.5 to 3dl/g and is a polymer of 0 to 20% acrylamide and 80 to 100% ionic monomer selected from diallyl dimethyl ammonium chloride, di-C₁₋₄ alkylaminopropyl (meth) acrylamide acid addition and quaternary ammonium salts and di-C₁₋₄ alkylaminoethyl (meth) acrylate acid addition and quaternary ammonium salts, an anionic flocculant is added to the suspension after the coagulant polymer, the particulate coagulant polymer is mixed into the suspension by flowing the suspension turbulently along duct means for not more than one minute to a position at which the flocculant is added, and the particulate coagulant polymer

substantially fully dissolves before the suspension reaches said position.

16. A process of separating suspended solids from coal tailings comprising:

5 providing water soluble beads having a size at least 90% from $30\mu\text{m}$ to $1,000\mu\text{m}$ of a polymer having intrinsic viscosity 0.5 to 3 dl/g formed from 80 to 100% diallyl dimethyl ammonium chloride and 0 to 20% acrylamide and that have a solubility such that upon mixing the particles into
10 the coal tailings they will substantially fully dissolve in less than about one minute,

mixing the polymer particles into the coal tailings as the coal tailings flow turbulently from a mixing position to a flocculant addition position that they reach after not
15 more than about one minutes flow time,

mixing anionic polymeric flocculant into the suspension at the flocculant addition position,

and then allowing sedimentation of the solids in the sedimentation vessel and thereby separating the solids from
20 the water of the coal tailings.

SUBSTITUTE SHEET