**Coal compositions and their production.**

A combustible friable fuel, e.g., for a power station boiler, is made by appropriate mixing of absorbent polymeric particles into a sticky coal fines filter cake. The friable fuel can be blended with coal smalls and then pulverised. The polymer is a cross linked, ionic, synthetic polymer.
Description

Coal Compositions and their Production

This invention relates to the utilisation of wet, sticky, coal fines filter cake in the production, by easy and safe techniques, of a product that can be used as, for instance, fuel for a power station, often after transportation in a truck.

Relatively large volumes of coal fines are formed during the mining of coal and during the recovery and transportation of mined coal. They have a size mainly below 0.5mm, and often considerably less. Some of the fines are separated from the coarse coal at the point of mining but others are washed from the coarse coal after mining. Irrespective of how they are separated, the coal fines cause a serious problem at a coal mine (underground or open cast). Normally they are put into the form of a mobile slurry or a froth flotation concentrate and are then converted into a filter cake by filtration, e.g., vacuum filtration by disc or drum filters. The filtration is performed to achieve the lowest possible water content but the final filter cake, when taken off the filters and subsequently handled, is always found to be a very sticky material that is highly viscous or is semi-solid. This very thick or semi-solid material is formed of wet coal fines and typically has a water content of around 30%. Its ash content is generally well below 30% based on solids, e.g., 10 to 15%.

Its texture is such that at present it is difficult to use any or all of it and vast volumes of the filter cake are dumped.

Attempts have been made to utilise it rather than dump it. For instance the sticky mass has been blended with coal smalls prior to use as a fuel. Unfortunately the fines are so sticky that they tend to clog the pulverisers, conveyors and other apparatus utilised for feeding the blend to the boiler. It is therefore essential to keep the amount of fines extremely low, generally not more than 10% of the total blend, and even at these low values results tend to be unsatisfactory.

Thermal or other water removal from the sticky mass would reduce many of these problems but, since the fines include substantial amounts below 100μm, the step of drying the fines (and the use of the resultant dried fines) would be liable to increase the flash hazard of the overall process.

It is already known to convert a wet particulate mass from a non-crumbly to a crumbly state by incorporating certain absorbent polymeric materials into the mass, for instance as described in EP 195550. A wide variety of wet particulate materials have been described as being treated by such processes. For instance in EP 195550 there are examples of treating wet lump coal having a particle size above 1cm and of treating filter coal tailings (i.e., the non-combustible tailings obtained during flotation of coal fines) having a size up to 1mm. No details are given of the mixing methods that are used.

Most of the literature is silent about the problems of treating coal fines filter cake, despite the enormous volumes of it that have been dumped and that are produced daily. An exception is GB 2,122,218 which describes a process in which wet filter cake fines were blended with coal smalls and the mixture was then blended with a binder such as cement followed by a polyelectrolyte such as the material sold under the trade name "Alcosorb ABl". Alcosorb ABl did not give adequate friability to the fines for sufficiently homogeneous mixing with coal smalls to permit use in non-pelletised form.

These problems could not have been overcome by the proposals in EP 195550. Even if those proposals had been applied to coal fines filter cake, there would still have been the problem that, when using the polymer particles proposed in EP 195550 in combination with conventional mixing methods, the improvement in friability of filter cake would have been beneficial but insufficient for commercial scale mixing with coal smalls as a pulverisable power station feed. Also there was still serious concern that pulverisation would lead to increased flash hazard or to clogging of the pulverisers or both. Accordingly the processes described in GB 2,122,218 and EP 195550 have not proved commercially useful for coal filter cake and there is still daily production and dumping of large volumes of wet, sticky, coal fines filter cake.

In the invention non-sticky, combustible, fuel is made from sticky coal fines filter cake by a process comprising mixing particulate absorbent polymer into the cake, and the process is characterised in that the polymer is a non-film forming, cross linked, synthetic polymer formed from water soluble ethylenically unsaturated monomer or monomer blend of which at least 5% by weight is ionic and the polymer is in the form of particles that are substantially non-sticky when swollen by water, and the mixing is conducted under conditions such that the cake is converted by the mixing from its sticky state to a friable form that can easily be blended substantially homogeneously with coal smalls.

It is essential in the invention that the friability of the treated cake is such that it can be blended substantially homogeneously with coal smalls, i.e., significant aggregates of sticky cake, generally free of smalls, are not
formed. This is a convenient indication that the filter cake has a friability suitable for a variety of purposes.

Since the product of the mixing is friable, instead of being a sticky mass, problems that have been encountered previously when blending up to 10% filter cake with smalls are avoided and, indeed, it is possible to use much larger amounts of filter cake in the blend, e.g., up to 20% or 30% based on the weight of the blend. The smalls can be any coal above 1mm, generally 2 to 10mm, but they can be larger.

Although the blend can be fed into power station boilers or other industrial combustion chambers in various physical forms, for instance in the form in which it is obtained by mixing, or after pelleting, it is generally preferred for the blend to be pulverised to a particle size below 200µm, often below 100µm, and for the resulting powder to be carried in an airstream into the power station boiler or other combustion chamber. Feed to the boiler often occurs continuously with the pulverisation, but in some instances the powder may be collected in hoppers and subsequently fed to the boiler. We have determined that the presence of swollen polymer does not cause clogging of the pulverisers.

Instead of blending the smalls after converting the cake to a friable form, some or all of the smalls can be included with the wet cake before addition of polymer.

Although the friable cake is suitable for blending with smalls, it is not essential to blend it with smalls and it can be used for a wide variety of other purposes. It may be bonded into pellets or other shaped bodies in ways known for bonding dry powder. Generally smalls are included in order to give a range of particle sizes. The friable cake, with or without blending with coal smalls and with or without a pulverisation step, may be used as a feed for, for instance a coke oven. For instance a blend of filter cake below 0.5mm and smalls 0.5mm to 15mm or more may be used as a feed to a coke oven, e.g., in a steel works.

The handling of pulverised coal and of coal fines is liable to incure a flash hazard unless suitable precautions are taken and the addition of fine particulate polymeric material, especially of the very fine particle sizes and oil dispersions that are preferred, would be contra-indicated because of the fear of increased flash hazard. However the evidence available to us shows that there is no increased flash hazard and that it is easily possible to pulverise, store and transport the friable cake safely, using conventional techniques.

A particular problem arises when friable filter cake is transported by truck since the inevitable vibration during transport tends to cause permanent caking or packing of a product that is otherwise sufficiently friable to be homogeneously mixed with coal smalls. Preferably therefore the friability is such that the friable cake does not pack seriously into a truck during transport, and can instead be easily tipped out of the truck after transport.

The filter cake generally has a water content of 20 to 40%, usually 25 to 35% and typically around 30%. The coal fines generally are substantially 100% below 0.5mm, often mainly in the range 50µm to 300µm and usually at least 80% by weight below 100µm, for instance 64% below 60µm. The ash content of the cake is usually below 30%, usually below 15%. The cake normally has the wet, sticky nature that is characteristic of conventional coal filter cake.

The filter cake may have been stored for short periods (e.g., in a truck) or for prolonged periods (e.g., in a dump) before blending with the polymer, but preferably the filter cake is blended with the polymer substantially continuously after formation of the cake. Cake formation is generally by vacuum filtration by a disc, drum or other vacuum filter of a slurry or froth flotation concentrate.

As mentioned above, it is known to convert a wet particulate mass into a friable form by mixing absorbent polymer particles into the mass, but the combinations of polymer, amount, particle size and mixing method that have been used previously would not have been effective for converting sticky coal fines filter cake into a friable form that can easily be blended substantially homogeneously with coal smalls. It has never previously been appreciated that it is, in fact, possible to convert the sticky filter cake to a suitable friable form by use of particular polymers and blending methods and that the resultant friable material can safely be pulverised with smalls or used in other ways as a feed for boilers, coking ovens or other purposes. It has also never previously been appreciated that the cake can be made so friable that it does not seriously pack during transport but can instead be easily tipped out of a truck after transport.

If the cake has a friable form that can easily be blended substantially homogeneously with coal smalls, the friable cake will have a substantially uniform texture throughout and can easily be crumbled between the fingers either into the individual coal fines or into small aggregates of, for instance, less than about 5mm and generally less than about 2mm. These small aggregates can themselves readily be crumbled between the fingers into smaller aggregates and eventually into substantially individual coal particles. This texture must exist substantially uniformly throughout the product since if it is non-uniform, and there are sticky areas within the product, then these sticky areas will interfere with the blending and other operations to which the fines are to be subjected. This manual crumbling test is therefore an easy preliminary way of determining whether the cake is sufficiently friable.

A convenient way of ascertaining whether a particular dosage of a particular particulate polymer can readily be used to provide the desired friable form is to measure the dissociation time and the shear dissociation time of that polymer dosage with the particular cake being used. For this purpose, the "dissociation time" is recorded by putting 600g of the coal filter cake in a Hobart mixer bowl, adding the water absorbent polymer, and stirring at speed 2 until the product becomes sufficiently friable that aggregates start being thrown out of the bowl. The time taken for this stage to be reached is the dissociation time and should generally be below 50 seconds, preferably below 30 seconds and most preferably below 15 or 20 seconds.

After stirring for a further 2 minutes at speed 1, the resultant mix is left for 30 minutes in a sealed bag, 100
grams of the mix is put into a cylinder 65mm in diameter and pressed into this cylinder to a disc under a
cake-forming pressure of 0.38kg/cm² (5.5psi) to give a cake. The cake is placed on a rectangular plate so that
the entire cake is within the profile of the plate, but a substantially semicircular portion is cut away from one
side of the plate so that about one third of the cake is unsupported. A solid plate is lowered at 12mm/sec on to
the top of the cake by a piston and is pressed down on to it with a pressure of 5psi (0.35kg/cm²). The time is
measured between the plate touching the top of the cake and the cake shattering over the cut away part of the
test plate. This is the shear dissociation time (SDT 5). If the cake shatters immediately upon contact with the
lowering plate, the shear dissociation time is recorded as zero.

SDT 5 needs to be below 30 seconds for generally satisfactory results and, in particular, if SDT 5 is below
about 20 seconds, preferably below about 10 seconds and most preferably below about 7 seconds (especially
substantially zero) and if the dissociation time is satisfactory, then the polymer cake combination is such that,
with appropriate mixing, homogeneous blendability with coal smalls can be expected. For instance Examples 1
and 2 below show that good results are obtained when SDT 5 is not above 7 and discussion is not above 18.

For the friable cake to resist caking or clogging during transport, a more friable texture is needed. For this,
the SDT test is repeated under a cake-forming pressure of about 20psi (1.4kg/cm²), to determine SDT 20, or
even at about 50psi (3.5kg/cm²) to determine SDT 50. These values also should be below about 20, preferably
below about 10, most preferably below about 7 seconds, especially substantially zero.

Having selected a potentially suitable combination of dosage, particle size and polymer type, it is then
necessary to ensure that the polymer is mixed very thoroughly and rapidly with the sticky cake. The polymer
must absorb water from the cake rapidly and uniformly. Most conventional mixing techniques are usually
inadequate and, in particular, plug mixing must be avoided as this will leave sticky zones within the cake.
Preferably therefore the mixing involves some degree of back mixing. This can be achieved by tumbling the
mass along a conveyor but preferably mixing is by one or more rotating members that provide both forward
and back mixing and that provide adequate shear. Preferred mixers are Simon or other double scroll mixers or,
especially, plough share mixers. Suitable plough share mixers are Lodige Mixers or Morton Mixers. A plough
share mixer has a substantially horizontal cylindrical container provided with a coaxial rotating shaft that
carries a plurality of mixing shovels each generally having the shape of a plough share and mounted to rotate
close to the wall of the cylinder. The peripheral speed and shape of the shovels causes the product to be
whirled from the particulate mass in the lower part of the cylinder into the free mixing zone above the mass, so
as to obtain high turbulence and both forward and back mixing.

The polymer can be added to the sticky mass by spraying or dusting, depending upon the form of the
polymer, and the mass then mixed in the defined manner. Mixing should be continued for as long as is
necessary to achieve thorough mixing, generally about 1/4 to 5 minutes. The mixer preferably operates
continuously.

A convenient way of determining whether the friability is such that the friable can be transported by truck
and then tipped or poured out of the truck without substantial clogging or caking is by testing with a Durham
Cone. A Durham cone is a cone of specified angle leading to an orifice of specified size incorporating a slide
valve. The cone is filled with 10-20kg coal and vibrated at a fixed speed. The vibration is then stopped and the
valve opened. If the friable coal fines flow evenly out of the cone, they are generally suitable for trucking without
caking. If they flow unevenly and tend to clog, they are not suitable for trucking.

The polymer particles must be substantially non-sticky when wet in order that they do not cause permanent
aggregation of the coal fines. The polymer preferably is substantially wholly insoluble (in the sense that very
little, and preferably none, dissolves from the particles into the cake, and preferably substantially none
solves from the particles upon stirring with water for 5 minutes). The polymerisation conditions and the
monomers used for making the polymer are preferably such that the content of high molecular weight linear, or
soluble, polymer is sufficiently low that during the process the particles do not become sticky. Typically the
amount of polymer that would dissolve out of the particles during 2 hours contact with 0.9% aqueous saline
solution is below 20%, preferably below 10%.

The polymer is made from water soluble monomer or monomer blend. The monomers are mainly
monoethylenically unsaturated, generally water soluble, monomers but cross linking agent is included in order
to convert the resultant polymer to water insoluble but water swellable form. The cross linking agent can be
reacted into the polymer after polymerisation but preferably is present during polymerisation. Generally it is a
di- or other poly- ethylenically unsaturated monomer such as methylene bis acrylamide or any of the other
ethylenically unsaturated cross linking agents that are suitable for cross linking absorbent polymer. Instead of
or in addition to relying on a covalent cross linking agent of this type, cross linking can also be through pendant
groups in known manner. For instance it can be by polyvalent metal ions.

The polymer is made from 5 to 100% anionic or cationic monomer and 0 to 95% non-ionic monomer. The
amount of ionic monomer is usually at least 10% by weight. The monomers are generally acrylic, but they can be
allylic or other vinyl monomers.

Suitable anionic monomers are ethylenically unsaturated carboxylic or sulphonic monomers such as (meth)
acrylic acid, allyl sulphonate or 2-acrylamido methyl propane sulphonic acid. Anionic monomers are generally
present as a water soluble salt, usually a sodium salt. Alkali metal salts are especially preferred.

Suitable non-ionic monomers are (meth) acrylamide and C1-4 alkyl (meth) acrylic esters, especially
hydroxyalkyl esters.

Suitable cationic monomers are dialkyl amino alkyl (meth) -acrylate or -acrylamide as free base, acid salt or,
preferably, quaternary salt and diallyl dimethyl ammonium chloride.

Cationic monomers are generally used as a blend with acrylamide. The amount of cationic monomer in the blend is often about 10 to 60% by weight. Anionic monomers may be present as homopolymer or as copolymers of anionic monomer with, preferably, acrylamide.

The polymers can be as described in EP 213795, or cationic versions thereof.

With some filter cakes, best results are achieved using cationic polymer alone or blends of cationic polymer with anionic polymer, but it is often preferred to use anionic polymer alone.

The preferred anionic polymers are cross linked polymers of about 5 to 100 mole % acrylic acid (as free acid or salt) with 0 to 95 mole % acrylamide and optionally 0 to 50 mole % other non-ionic or anionic monomer. The acrylic acid is preferably present as sodium salt, i.e., wholly or mainly (e.g., at least 70 or 80% by weight) as sodium acrylate. Suitable polymers are copolymers in which the amount of acrylic acid (as free acid or salt) is typically from about 10 or 20 to 75% by weight, with the balance being acrylamide. It is generally preferred for least 40% by weight of the monomers for the anionic polymer to be sodium acrylate. Typical polymers of this general type are cross linked polymers of about 40 to 60% by weight sodium acrylate with 60 to 40% by weight acrylamide.

Particularly preferred swellable polymers for use in the invention are acrylic acid sodium salt homopolymers, although up to 20% of the sodium acrylate can be replaced by acrylamide. Some of the acrylate groups usually are in the form of acrylic acid or other water soluble salts, generally other alkali metal salts.

The degree of swellability and absorption is controlled, in part, by the extent of cross linking and the amount of cross linking agent is usually below about 500 ppm, often below 300 ppm. It is usually at least 10 ppm or 20 ppm and preferably at least 50 ppm. Best results are often achieved at around 100 or 200 ppm. These amounts are the amounts by weight of monomer of methylene bis acrylamide and equivalent amounts of other cross linking agents may be used.

The degree of cross linking, and the polymer type, should be such that the gel capacity of the polymer (grams deionised water absorbed per gram dry polymer) is at least about 25, generally at least 100 and preferably at least 200 typically up to 500 or even 700 or higher.

In some instances it is desirable for the polymer particles to have a surface layer that is less swellable than the inner parts of the particles. The desired reduced swellability of the surface layer is preferably obtained by cross linking the surface layer. This reduces the content of linear polymer at any position where it might cause stickiness and has the advantage of promoting uptake of water and of preventing aggregation of the polymer particles. The desired surface cross linking can be achieved by methods such as those described in U.S. 3,114,651, 3,251,814, 4,043,952, 4,093,013 and 4,090,013, JP 1983/42602 and EP 227305. Other ways of treating the surface are by applying a coating of a counter ionic polymer (e.g., poly diallyl dimethyl ammonium chloride or other cationic polymer when the swellable polymer is anionic) or by applying sodium aluminate or other aluminate.

The polymer particles can be relatively large, e.g., up to 0.5mm or even 1mm or up to 2mm, but the degree and duration of mixing that is necessary generally increases as the particle size increases. For most purposes it is therefore generally desirable for the particles to have a size during the mixing step of below 300μm and generally below 200μm and preferably at least 50% of the particles have a size during the mixing step below 50μm. However when the greatest degree of friability is required (e.g., to resist caking during trucking) it is surprisingly best to use larger particles (e.g., 100-300μm or even up to 1 or 2mm) with sufficiently prolonged mixing.

In particular we find with conventional comminuted or bead polymer particles that, as the polymer size increases, potential friability can increase and the risk of polymer overdosing decreases. At lower particle sizes (e.g., below 125μm), adequate friability for homogeneous blending with coal smalls can be obtained in the invention. However caking may be a problem during trucking of the friable product due to it being insufficiently friable to resist the effect of vibration (e.g., SDT 5 < 10 but SDT 20 > 20 seconds). Mixing can be fairly quick (dissociation below 20 seconds), but friability is very dose sensitive in that SDT 5 deteriorates quite markedly either side of a fairly narrow range of optimum doses. At coarser particle sizes, greater doses and longer mixing times are needed (dissociation times up to 50 seconds and sometimes even up to 120 seconds) but the friability is better (SDT 20 < 20 seconds and often < 10 seconds) and there is less risk of overdosing.

The polymer particles may be introduced as individual particles having the size that is required during the mixing step or they may be introduced as aggregates that we assume break down during the mixing step into smaller particles that have the desired size during the mixing.

If particles below 50μm are introduced into the mixing step in the form of free powder, the handling of the particles can cause dusting problems and the system is dose sensitive and SDT 20 may be rather high. We have surprisingly found that it is possible to combine the lower dosages and the fast mixing characteristics of small particles with the improved friability and reduced risk of overdosing, and avoidance of dusting problems, of large particles by introducing the polymer in the form of powder having a particle size above 50μm and which consists of internally bonded aggregates of finer particles having a size of below 50μm and often below 30μm. For instance polymer gel fines, e.g., as obtained from the comminution of polymer gel or as fines from a reverse phase bead polymerisation process, can be aggregated by swelling with sufficient water to form a comminutable gel, comminuted to a coarse size and dried (e.g., by a fluidised bed). These internally bonded aggregates appear to behave initially as coarse particles and then to behave as fines.

Any aqueous solution that permits swelling can be used. Water is usually best. An aqueous solution of a
small amount of a soluble polymer or other binder could be used. The comminution can be to > 90% by weight above 50μm and usually above 100μm, but generally below 1 or 2mm and often below 500μm. Commination can be by conventional gel comminution methods. Drying can be by conventional techniques followed, if necessary, by comminution in conventional manner. The resultant aggregates have a size in the range generally of 50 to 500μm. They can very satisfactorily be used in the invention. The fines within each aggregate typically have a size mainly 5 to 30μm and often below 20μm.

By swelling the fines into a comminutable gel, the resultant dried comminuted particles appear to be internally bonded. This is in contrast to the skin bonding effect that is obtained if fines are merely sprayed with water and immediately dried in a fluid bed. Skin bonded aggregates can be used in the invention but internally bonded aggregates give better results. They are novel materials.

Another effective way of incorporating the preferred particles having at least 90% by weight below 50μm is as a dispersion in water-immiscible liquid.

Preferably at least 90% of the particles are below about 20μm or 30μm, and most preferably below 10μm. Fastest results are generally achieved with at least 90%, preferably 99%, by weight being below 3μm, e.g., in the range 0.03 to 2μm. Often however adequate results are obtained in a cost effective manner, albeit more slowly, if the particle are 90% between 5 and 50μm, e.g., about 5 to 30μm.

Whereas most industrial processes that use dispersions of polymer in water-immiscible liquid require that the amount of polymer should be as high as possible, in the invention we find that best results are achieved when the amount of polymer is relatively low. Thus although the dry weight of polymer can be up to, for instance, 50 or 60% by weight of the dispersion, the dry weight of polymer in the dispersion is preferably below 40% by weight and preferably below 40%. Generally it is at least 15%, preferably at least 20%. Concentrations of 30 to 40% polymer dry weight based on total dispersion are often best when the polymer particles are wet and 20 to 30% when the polymer particles are dry.

The water-immiscible liquid may be any organic liquid in which the polymer particles can be adequately dispersed and that will not interfere with the process and so in practice needs to be substantially water immiscible. It can be, for instance, a vegetable oil but is preferably a hydrocarbon or halogenated hydrocarbon liquid. It may be selected from any of the liquids conventionally used in reverse phase dispersions. For instance it can be kerosene or diesel oil or other mineral oil.

The dispersion can be formed at the point of use, with the polymer particles being dispersed into the water-immiscible liquid and the mixture then being applied substantially immediately to the wet particulate mass. Preferably however the dispersion is preformed, in which event it needs to be substantially stable against settlement.

One form of dispersion is a suspension obtained by dispersing preformed dry polymer particles into water-immiscible liquid in the presence of a dispersion stabiliser. The preformed dry polymer particles can be reverse phase microbeads but preferably they are fines separated from polymer gel, e.g., obtained during the comminution of bulk or bead gel or separated from beads obtained by reverse phase polymerisation.

The amount of stabiliser is generally from 1 to 15%, often 3 to 10%, by weight based on the dry weight of polymer. Conventional stabilisers for oil based dispersions may be used, e.g., Bentone clays but preferably the dispersion is stabilised by stirring into it an aqueous emulsion of an oil soluble or oil swellable polymeric thickener, generally a thickener that is insoluble and non-swellable in water. Suitable thickeners are described in EP-A-0161926, for instance in Example 7 and at page 11 line 22 to page 12 line 10.

Instead of using polymer fines, typically having a size of 10 to 30 or 10 to 40μm, the dispersion can be a reverse phase dispersion made by reverse phase polymerisation of aqueous monomer or monomer blend in water-immiscible liquid. See for instance U.S. 4,059,552. The reverse phase polymerisation is preferably conducted as a reverse phase suspension polymerisation. Formation of an initial dispersion of monomer particles can be facilitated by the incorporation of a small amount of water-in-oil emulsifying agent. Often amphipathic stabiliser is included, in known manner, especially when the dispersion is subsequently azeotroped. Depending upon the degree of agitation when forming the initial dispersion of aqueous monomer in the non-aqueous liquid, and depending upon the amount and type of stabiliser and emulsifier, if present, the dry particle size of the final dispersion can be controlled and typically has a maximum size of 1μm or up to 2 or 3μm or 10μm at the most. The product of the reverse phase polymerisation can be described as an emulsion. It may be dried, e.g., by azeotroping to reduce the water content, typically to below 15% by weight of the polymer. The product is then a substantially dry dispersion.

The amount of amphipathic stabiliser (if present) is generally in the range 0.2 to 0.5 to 10%, and generally below 5%, based on the weight of polymer. The amount of water-in-oil emulsifier is preferably from 0.2 to 3%, based on weight of monomer.

In normal processes in which a dispersion in oil of water soluble or swellable polymer is mixed into water, it is conventional to conduct the mixing in the presence of an oil-in-water emulsifier so as to promote distribution of the dispersion and the dispersed polymer into the water. For instance, it is common to add the emulsifier to the polymer dispersion before blending with the water. Because of the apparent need to achieve rapid distribution of the polymer throughout the wet particulate mass, we therefore expected it to be necessary to use such an emulsifier. We have surprisingly found, in the invention, that better results are achieved in the absence of this emulsifier than when the conventional addition is made. This suggests, surprisingly, that it is desirable to retard the rate at which the polymer particles are made available to, and can take up water from, the wet filter cake.
Since one purpose of the polymer particles is to absorb water from the wet filter cake it would be expected that the particles should be as dry as possible at the start of the process. However we have surprisingly found that improved results are achieved when, at the time of addition to the wet particulate mass, the polymer particles in the dispersion contain a substantial amount of water, usually at least 30% based on the dry weight of polymer. Usually the amount is below 150% and typically is in the range 60 to 120%, preferably 80 to 100%, based on the dry weight of polymer.

Preferred compositions comprise 20 to 50% by weight of each of the polymer (dry weight), water-immiscible liquid and water. The amount of each of the polymer and the water immiscible liquid is preferably 25 to 45%, most preferably 30 to 40% by weight. The amount of the water is preferably from 20 to 40%, most preferably 25 to 35%. Particular preferred compositions comprise 30 to 40% by weight polymer, 30 to 40% by weight water immiscible liquid and 25 to 35% by weight water, with the amount of water generally being less than the weight of polymer.

Compositions containing such amounts of water tend to be unstable if the dry particle size is significantly above 10μm and so the preferred compositions that contain water have a particle size lower than this, preferably below 3μm. They can be made by reverse phase polymerisation (usually by reverse phase suspension polymerisation) to form an emulsion of aqueous polymer gel particles dispersed in the water immiscible liquid, and then the emulsion can be used as such without further drying and without the addition of oil-in-water activator. However for some purposes it appears best to dry the emulsion by azotroping in conventional manner and then to add water back into the dispersion.

It is very surprising that better results can be achieved using wet polymer particles than dry, both because it would be expected that dry particles would be more effective absorbents and because it has occasionally been suggested in the literature that wet particles initiate absorption quicker than dry particles. However the improved results obtainable in the absence of oil-in-water emulsifier indicate that accelerated absorption is not desirable.

When the polymer particles are large, such that the swollen polymer particles have a size greater than the size of most or all of the coal fines, the swollen polymer particles can subsequently be separated from the dry coal fines. For instance in one process according to the invention at least 50% (dry weight) of the swollen polymer particles have a size greater than the size of at least 95% of the substantially dry coal fines and these oversize swollen particles are separated from the dry coal fines. Preferably the polymer particles swell to at least twice their dry diameter and substantially all the said swollen polymer particles have a size greater than the size of substantially all the dry coal fines and the polymer particles are separated from the dry coal fines. The separation may be by conventional size classification or weight classification techniques, preferably by sieving using a vibrating sieve.

The dry coal fines are subsequently used as fuel and as a result of having separated the polymer from the fines the water content of the polymer is not carried in to the fuel and the separated swollen particles can, if desired, be dried (e.g., by heat exchange from the fuel burner) and can be recycled for further use.

The swellable polymer particles may be mixed with the wet filter cake without any prior addition of any material to the filter cake. However improved results can be achieved if the filter cake that is mixed with the swellable polymer particles have previously been treated with a co-ionic dispersing agent, a counter-ionic coagulant, or a co-ionic, counter-ionic or non-ionic flocculant. ("Counterionic" means that the agent is cationic when the swellable polymer is anionic, and vice versa.) For instance the wet filter cake may be blended with a solution of the dispersing agent, coagulant or flocculant so as to promote liberation of bound water from the cake, before adding the absorbent polymer particles. In some instances it can be desirable to include the dispersing agent with the swellable polymer at the time of a filtration stage, e.g., for producing the wet filter cake. For instance a slurry or froth concentrate of the coal fines can be treated by a coagulant or a flocculant or a combination (usually a coagulant followed by a flocculant) prior to filtration to provide the wet filter cake.

Co-ionic dispersing agent is generally a polymer of low molecular weight, usually below 500,000, generally below 200,000 and often below 50,000. For many processes molecular weights of below 10,000, e.g., 2,000 to 5,000, are satisfactory. The dispersing agent is usually anionic. The counter-ionic coagulant generally has a molecular weight of above 50,000, often in the range 100,000 to 1 million, typically about 500,000. However it can have a higher molecular weight. The flocculant can have molecular weight below 1 million but generally it is above. It can be of several million, and can be of typical flocculant molecular weight.

Although these polymeric agents are usually substantially linear and are applied in true solution, it can be particularly advantageous, especially when the agent is a higher molecular weight agent such as a flocculant, for the agent to be in the form of very small particles at the time it is mixed with the coal fines, preferably being a slightly cross linked flocculant polymer. For instance it may be as described in EP 0202780.

The added agents are usually synthetic polymers formed from water soluble ethylenically unsaturated monomers, and these monomers will be chosen to give the polymer the desired ionic characteristic. They may be any of the anionic, cationic and non-ionic monomers listed above for the swellable polymer. The cationic dispersing agent is preferably a low molecular weight polymer of diallyl dimethyl ammonium chloride or dimethyl amino ethyl (meth) acrylate, or a blend of either of these with acrylamide.

It is often preferred that the particle sizes and the amounts of the absorbent polymer and of the filter cake are such that the number ratio of swellable polymer particles:filter cake particles is approximately 1, e.g., from 3:1 to 1:3. For instance this is achieved by adding about 0.2% (dry on dry) of polymer particles having a particle size of about 20 to 30μm to filter cake having a particle size of about 100μm. Larger amounts of these polymer
particles are appropriate when the filter cake has a significant electrolyte content.

The amount of absorbent polymer that is applied is generally at least 0.005% and is preferably at least 0.05%. It is usually below 5%, preferably below 1% and most preferably is around 0.05 to 0.5%. It is a particular advantage of the invention that, despite the unpleasant sticky character of the filter cake, good results can be obtained with very low amounts of polymer, often below 0.3% or 0.4% and often below 0.15% or 0.2%. These amounts are of dry polymer based on dry particles by weight.

The following are some examples.

Example 1

Sodium polyacrylate cross linked with 0.025% methylene bis acrylamide is formed by conventional bulk gel polymerisation and is dried and comminuted in conventional manner. The resultant particles are classified according to size and the fines are retained for use in the invention. They have a dry particle size below 50µm, mainly in the range 10 to 30µm.

The fines are dispersed into an equal weight of a hydrocarbon oil that is thickened with a dispersion stabiliser as described at page 18 lines 25 to 35 of EP 0161926A. 1% oil-in-water emulsifier is included.

The dispersion is sprayed onto to a wet filter cake of coal fines, this filter cake having been taken from a vacuum filter following froth flotation. The amount of dispersion is 0.1% dry polymer on dry particulate mass. The product is mixed thoroughly and rapidly becomes a friable, crumbly solid. This can easily be blended with coal smalls to form a fuel. Without the addition of the dispersion, the filter cake is a wet sticky mass that could not easily be used.

In a comparison, when a similar amount of dry polymer particles of the same polymer but having a size of around 100µm, and that are not dispersed in oil, was added to the cake, the cake does not become so crumbly so quickly. With prolonged mixing and larger amounts of polymer (e.g. 0.2% or even 0.5%) the product is adequately crumbly but swollen polymer particles and aggregates are apparent.

Example 2

Three types of dispersion, each containing equal amounts of polymer and hydrocarbon oil (kerosene or diesel), and oil-in-water emulsifier, are made as follows.

Suspensions - by the general technique of Example 1 using particles of the size shown, with >90% by weight <50µm. RP Emulsions - by the reverse phase polymerisation to give a product of about 35% oil, 35% polymer, 30% water RP Dispersions - by azeotroping RP Emulsions to about 50% polymer 50% oil

The compositions are tested at 0.5% product on wet coal filter cake as above. The monomers used and the results are in the following table, where NaAc = % sodium acrylate, ACM = % acrylamide and MBA = methylene bis acrylamide (ppm).
<table>
<thead>
<tr>
<th>Composition</th>
<th>NaAc</th>
<th>ACM</th>
<th>MBA</th>
<th>Dissociation</th>
<th>SDT 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ex 1</td>
<td>100</td>
<td>0</td>
<td>200</td>
<td>18</td>
<td>7</td>
</tr>
<tr>
<td>355-500μm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Suspension</td>
<td>50</td>
<td>50</td>
<td>200</td>
<td>82</td>
<td>0</td>
</tr>
<tr>
<td>65-180μm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Suspension</td>
<td>50</td>
<td>50</td>
<td>200</td>
<td>28</td>
<td>0</td>
</tr>
<tr>
<td>&lt;65μm Suspension</td>
<td>50</td>
<td>50</td>
<td>200</td>
<td>14</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RP Dispersion</td>
<td>50</td>
<td>50</td>
<td>100</td>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>do.</td>
<td>50</td>
<td>50</td>
<td>200</td>
<td>37</td>
<td>0</td>
</tr>
<tr>
<td>do.</td>
<td>50</td>
<td>50</td>
<td>300</td>
<td>75</td>
<td>0</td>
</tr>
<tr>
<td>do.</td>
<td>25</td>
<td>75</td>
<td>25</td>
<td>30</td>
<td>+30</td>
</tr>
<tr>
<td>do.</td>
<td>25</td>
<td>75</td>
<td>50</td>
<td>42</td>
<td>11</td>
</tr>
<tr>
<td>do.</td>
<td>25</td>
<td>75</td>
<td>100</td>
<td>32</td>
<td>0</td>
</tr>
<tr>
<td>do.</td>
<td>25</td>
<td>75</td>
<td>200</td>
<td>40</td>
<td>0</td>
</tr>
<tr>
<td>RP Emulsion</td>
<td>100</td>
<td>0</td>
<td>100</td>
<td>31</td>
<td>4.2</td>
</tr>
<tr>
<td>RP Dispersion</td>
<td>100</td>
<td>0</td>
<td>100</td>
<td>25</td>
<td>14</td>
</tr>
</tbody>
</table>

It is apparent from this that some of the exemplified processes require rather long mixing times because the dissociation time is rather high for satisfactory results. However it is also apparent from these examples that it is easy to achieve satisfactory results by, for instance, reducing the particle size from above 355μm to below 180μm or by increasing the proportion of sodium acrylate. It is also apparent that if the amount of cross linking agent is too low (25ppm in this example), SDT 5 is too high. This is probably due to the polymer containing too much soluble polymer, thus rendering it sticky.

Example 3
Tests similar to Example 2 are conducted on RP dispersions of 50% oil and 50% of a copolymer of 50% NaAc 50% ACM 200 ppm MBA with or without added oil-in-water emulsifier, at different amounts of polymer.
The disadvantage of incorporating emulsifier is apparent.

Example 4
Tests similar to Example 2 are conducted on a 50% RP dispersion of a copolymer of 50% NaAc 50% ACM 200 ppm MBA (product A) and the same product after dilution to 25% polymer by red diesel oil (B).

The benefit of reducing the polymer concentration is apparent.

Example 5
A RP dispersion is formed of 50% oil 50% copolymer of 50% NaAc 50% ACM 200 ppm MBA. This is diluted with various amounts of water and the products are tested on wet coal filter cake as in Example 2 at different dosages of product.
| Product | Amount | Polymer % | Water % | Oil % | Dissociation | SDT  
|---------|--------|-----------|---------|-------|--------------| 
| 0.5%    | 50     | 0         | 50      |       | 19           | 3.4  
| 0.2%    | 50     | 0         | 50      |       | 31           | 30   
| 0.56%   | 45     | 10        | 45      |       | 31           | 4.8  
| 0.22%   | 45     | 10        | 45      |       | 34.6         | 10.6 | 
| 0.63%   | 40     | 20        | 40      |       | 24.9         | 3.8  
| 0.25%   | 40     | 20        | 40      |       | 31.8         | 8.9  
| 0.71%   | 35     | 30        | 35      |       | 24.1         | 2.4  
| 0.29%   | 35     | 30        | 35      |       | 29.9         | 14.4 | 
| 0.83%   | 30     | 40        | 30      |       | 22.5         | 2.9  
| 0.33%   | 30     | 40        | 30      |       | 26.8         | +30  
| 1.0%    | 25     | 50        | 25      |       | 22.6         | 3.9  
| 0.4%    | 25     | 50        | 25      |       | 29.7         | +30  

This clearly shows that the addition of a controlled amount of water gives improved results at low dosages and thus provides a particularly cost effective system.

Example 6

Example 2 is repeated using similar amounts of three different polymer suspensions. Tests 2-4 are with 60% dispersions in oil and tests 5-7 are with 50% dispersions in oil. Test 8 is with 1% of a 25% emulsion of aqueous polymer particles in oil and test 9 with a 50% dry dispersion of similar, but dry, polymer particles. The unsatisfactory results from non-ionic polymer are shown in test 7.

| Test | Polymer  | ppm MBA | Amount | Dissociation | SDT  
|------|----------|---------|--------|--------------|------ 
| 1    | 100 NaAc | 200     | 0.5%   | 18           | 4.6  
| 2    | 25 NaAc  | 75 ACM  | 100    | 0.4%         | 20.3 | 3.4  
| 3    | 20 NaAc  | 80 ACM  | 100    | 0.4%         | 25.6 | 2.6  
| 4    | 10 NaAc  | 90 ACM  | 100    | 0.4%         | 29.8 | 2.4  
| 5    | 50 NaAc  | 50 ACM  | 200    | 0.5%         | 37.6 | 0    
| 6    | 25 NaAc  | 75 ACM  | 200    | 0.5%         | 40.5 | 0    
| 7    | 100 ACM  | 200     | 0.5%   | 39.4         | +30  
| 8    | 50 NaAc  | 50 ACM  | 100    | 1%           | 23.0 | 3.9  
| 9    | 50 NaAc  | 50 ACM  | 100    | 0.5%         | 22.4 | 2.9  

Example 8

The process of example 2 is repeated but using a 35% by weight RP emulsion in oil of cationic swellable polymer formed from 60% ACM 40% dimethylaminoethyl acrylate (MeCl quaternary salt). At 1% dosage, Dissociation is 11.7 seconds and SDT 5 is 0.9. When using a 1% polymer dosage of a 50% RP dispersion of a swellable polymer of 50% ACM 50% NaAc (instead of the cationic polymer). Dissociation is 11 and SDT 5 is
Example 9
An aqueous solution of cationic soluble polymer A, B or C is stirred into a wet filter cake of coal fines. After stirring for one minute, a 50% dispersion in oil of cross linked gel polymer particles of acrylamide and sodium acrylate polymer is blended into the filter cake. The results are as follows, in which polymer A is a low molecular weight diallyl dimethyl ammonium chloride coagulant, polymer B is a high molecular weight, slightly cross linked, copolymer of 58 mole percent acrylamide and 42 mole percent cationic dialkylaminoalkyl acrylate quaternary monomer, and polymer C is a homopolymer of a cationic dialkylaminoalkyl methacrylate quaternary monomer. In addition to the results shown in the table below, the product was assessed visually and it is significant that increasing amounts of product B, and especially the tests with product C, give the best visual appearance.

<table>
<thead>
<tr>
<th>% Cationic Polymer</th>
<th>% Dispersion</th>
<th>Dissociation</th>
<th>SDT 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.5</td>
<td>18.4</td>
<td>6.7</td>
</tr>
<tr>
<td>0.05 A</td>
<td>0.5</td>
<td>19.6</td>
<td>3.1</td>
</tr>
<tr>
<td>0.15 A</td>
<td>0.5</td>
<td>17.5</td>
<td>3.6</td>
</tr>
<tr>
<td>25</td>
<td>1.0</td>
<td>17.5</td>
<td>2.6</td>
</tr>
<tr>
<td>0.15 A</td>
<td>1.0</td>
<td>16.9</td>
<td>0</td>
</tr>
<tr>
<td>0.3 A</td>
<td>1.0</td>
<td>15.2</td>
<td>1.9</td>
</tr>
<tr>
<td>30</td>
<td>1.0</td>
<td>17.5</td>
<td>2.6</td>
</tr>
<tr>
<td>0.08 B</td>
<td>1.0</td>
<td>12.1</td>
<td>2.0</td>
</tr>
<tr>
<td>0.16 B</td>
<td>1.0</td>
<td>10.9</td>
<td>0</td>
</tr>
<tr>
<td>35</td>
<td>1.0</td>
<td>17.5</td>
<td>2.6</td>
</tr>
<tr>
<td>0.4 C</td>
<td>1.0</td>
<td>8.7</td>
<td>0</td>
</tr>
<tr>
<td>0.8 C</td>
<td>1.0</td>
<td>8.6</td>
<td>0</td>
</tr>
</tbody>
</table>

Example 10
Fines having a size mainly 10-30μm are separated from comminuted cross linked polyacrylic acid (75% as sodium salt) gel having a gel capacity well in excess of 25g/g. They are labelled A. Part of them are mixed with sufficient water to make a comminutable gel which is then comminuted and dried on a fluid bed drier, in conventional manner, to a particle size > 125μm but below 500μm. This is labelled B. Each product is mixed with coal filter cake as in Example 1 at various doses.
<table>
<thead>
<tr>
<th>Product</th>
<th>Dose (1%)</th>
<th>Dissociation Time (sec)</th>
<th>SDT 5</th>
<th>SDT 20</th>
<th>SDT 50</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.25</td>
<td>13.1</td>
<td>2.7</td>
<td>30+</td>
<td>30+</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>9.9</td>
<td>1.3</td>
<td>4.7</td>
<td>30+</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>8.3</td>
<td>0.7</td>
<td>2.9</td>
<td>30+</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>7.9</td>
<td>0.9</td>
<td>2.9</td>
<td>30+</td>
</tr>
<tr>
<td>B</td>
<td>0.25</td>
<td>23.2</td>
<td>1.5</td>
<td>30+</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>14.8</td>
<td>0</td>
<td>2.0</td>
<td>30+</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>13.1</td>
<td>0</td>
<td>0</td>
<td>3.6</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>12.5</td>
<td>0</td>
<td>0</td>
<td>2.1</td>
</tr>
</tbody>
</table>

This demonstrates that the agglomerates give improved results at higher dosages but give similar results at lower dosages.

Example 11

Products A, B and C are formed from 50% ACM 50% NaAc cross linked swellable polymer having gel capacity above 25g/g. A is a dispersion in oil of particles <40µm. B is powder <63µm and C >125µm. Different amounts are blended as in Example 1. The results are as follows.
<table>
<thead>
<tr>
<th>Product</th>
<th>Active Dose (1%)</th>
<th>Dissociation Time (sec)</th>
<th>SDT 5</th>
<th>SDT 20</th>
<th>SDT 50</th>
</tr>
</thead>
<tbody>
<tr>
<td>A &lt;40μm</td>
<td>0.15</td>
<td>15.6</td>
<td>2.7</td>
<td>30+</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>12.5</td>
<td>1.7</td>
<td>30+</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>9.8</td>
<td>2.5</td>
<td>30+</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>8.1</td>
<td>2.4</td>
<td>30+</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>7.4</td>
<td>2.7</td>
<td>30+</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>5.9</td>
<td>2.5</td>
<td>30+</td>
<td></td>
</tr>
<tr>
<td>B &lt;63μm</td>
<td>0.15</td>
<td>20.8</td>
<td>30+</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>12.2</td>
<td>2.7</td>
<td>30+</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>8.9</td>
<td>1.2</td>
<td>3.1</td>
<td>30+</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>8.2</td>
<td>0</td>
<td>3.5</td>
<td>30+</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>7.2</td>
<td>0</td>
<td>3.8</td>
<td>30+</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>6.6</td>
<td>0</td>
<td>3.9</td>
<td>30+</td>
</tr>
<tr>
<td>C &gt;125μm</td>
<td>0.15</td>
<td>25.4</td>
<td>30+</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>15.7</td>
<td>1.0</td>
<td>5.6</td>
<td>30+</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>10.9</td>
<td>0</td>
<td>0</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>9.5</td>
<td>0</td>
<td>0</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>9.3</td>
<td>0</td>
<td>0</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>7.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

This again shows that low particle sizes give satisfactory dissociation and SDT 5 values at low dosages but inadequate SDT 20 values, but also shows that there is an optimum low dose. It also shows that although large particle sizes give good SDT 20 and SDT 50 values at high doses, the results are not acceptable at lowest doses. Also the benefits of the large particles are not lost when the dose is increased further. Comparison with Example 11 shows the benefits of using agglomerates rather than conventional particles of similar size.

**Example 12**
Three grades of cross linked powdered acrylamide polymers, containing different amounts of sodium acrylate groups, are tested as in Example 1. The 3% anionic grade is the product commercially available as Alcosorb ABI and is more properly regarded as non-ionic.
This clearly demonstrates that the non-ionic product gives, at equivalent dosage, greatly inferior results compared to the more highly anionic grades used in the invention.

Example 13

Polyacrylic acid (about 75% in sodium form) gel cross linked with about 200ppm MBA is formed, comminuted and dried in conventional manner. Fines having a size mainly in the range 10 to 40μm are separated and dispersed at 50% solids in kerosene or diesel using an emulsion of stabilising polymer (as in EP-A-0161926, Example 7) as stabiliser.

The resultant dispersion is diluted to about 25% solids with further kerosene or diesel and sprayed at about 0.2% polymer on to coal filter cake having a coal size mainly 50 to 150μm and a moisture content around 30% and an ash content of around 10% as the cake is fed into a continuously moving Lodge Plough Share mixer.

The mix passes through the mixer in not more than about 2 minutes and emerges as a friable product that can easily be crumbled between the fingers (the SDT 5 for the wet filter cake-polymer combination is below 10).

The friable product is blended with about 5 times its own weight of coal smalls having a size of 1 to 10mm and the mix is pulverised and carried, entrained in air from the pulverisers, as a fuel into the combustion chamber of a power station boiler. There is no evidence of clogging of the pulverisers or other parts of the apparatus through which the product travels from the mixer to the boiler.

The blend, before pulverisation, may flow evenly out of a Durham Cone at that is uniform and is about 1.4kg/sec, whereas the untreated cake clogs or flows unevenly at about half that rate.

Claims

1. A process for making a non-sticky, combustible, fuel from sticky coal fines filter cake comprising mixing particulate absorbent polymer into the cake, characterised in that the polymer is a non-film forming, cross linked, synthetic polymer formed from water soluble ethylenically unsaturated monomer or monomer blend of which at least 5% by weight is ionic and the polymer is in the form of particles that are substantially non-sticky when swollen by water, and the mixing is conducted under conditions such that
the cake is converted by the mixing from its sticky state to a friable form that can easily be blended substantially homogeneously with coal smalls.

2. A process according to claim 1 in which the resultant friable mass is blended with coal smalls.

3. A process according to claim 1 or claim 2 in which the polymer is a cross linked polymer formed from anionic or cationic ethylenically unsaturated monomer optionally mixed with non-ionic monomer and has gel capacity of at least 25 grams dionised water per gram polymer.

4. A process according to any preceding claim in which the polymer is a cross linked polymer of 10 to 100% acrylic acid sodium salt and 0 to 90% acrylamide.

5. A process according to claim 4 in which the polymer is formed of 0-20% acrylamide and 80-100% acrylic acid sodium salt.

6. A process according to any preceding claim in which the surface of the polymer particles is preferentially cross linked.

7. A process according to any preceding claim in which the polymer particles have at least 90% by weight below 50µm and are added to the cake in the form of a dispersion in water immiscible liquid.

8. A process according to claim 7 in which the dispersion is a dispersion of fines obtained from polymer gel.

9. A process according to claim 8 in which the dispersion is stabilised against settlement as a result of the incorporation into the dispersion of an oil swellable or oil soluble polymeric thickener.

10. A process according to claim 7 in which at least 90% by weight of the polymer particles have a dry size below 10µm and the dispersion has been obtained by reverse phase polymerisation.

11. A process according to any preceding claim in which the particulate polymeric material, its amount and the filter cake are such that the dissociation time, as defined herein is not above 18 seconds and SDT 5, as defined herein, is not above 7 seconds.

12. A process according to claim 7 in which at least 90% by weight of the particles have a dry size below 10µm and a dispersion contains at least 30% by weight water.

13. A process according to claim 7 in which the dispersion is made by reverse phase polymerisation and comprises 5 to 45% by weight of the polymer particles, 45% by weight water and 25 to 45% by weight water immiscible liquid, and the polymer particles have a dry size below 10µm.

14. A process according to claim 7 in which the dispersion is substantially free of oil-in-water emulsifier.

15. A process according to any preceding claim in which the mixing is by a double scroll or plough share mixer.

16. A process according to any preceding claim in which the mixing is conducted substantially continuously using a plough share mixer.

17. A process according to any of claims 1 to 6 in which the polymer particles are added to the mixture while having a size mainly above 125µm.

18. A process according to claim 17 in which the polymer particles are added to the mixture as internally bonded agglomerates having a size mainly above 125µm and formed of fines having a size mainly below 30µm.

19. A process according to claim 17 or claim 18 in which SDT 20, as herein defined, is below 20.

20. A process according to any of claims 17 to 19 in which the mixing is by a plough share mixer.

21. A process according to any preceding claim in which the particulate polymeric material, its amount and the filter cake are such that SDT 5, as defined herein, is below 20 and dissociation, as defined herein, is below 50 seconds.

22. A process according to claim 21 in which the polymer particles have at least 90% by weight below 50µm and are added to the cake in the form of a dispersion in a water immiscible liquid.

23. A process according to any preceding claim in which the filter cake is taken from a stack of dumped filter cake.

24. A process according to claim 22 in which the filter cake is taken from a stack of dumped filter cake.

25. A process according to any preceding claim in which the friable product is blended with coal smalls in an amount of at least 10% and the blend is pulverised and carried in an airstream, optionally after storage, into a combustion chamber where it is burnt.

26. A process according to claim 1 substantially as herein described with reference to any of the Examples.