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PROCESS OF CLASSIFYING MINERALS

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The invention relates to inhibiting the adhesion of carbonaceous solids and organic liquids and to preventing transportation of organic parting liquid on the surface of minerals. More particularly the invention is for some uses an improvement over the process described in the copending application of Alexander, du Pont and Foulke, Serial No. 177,190, and finds particular application in the separation of coal from indigenous impurities. The process will be described in its application to soft coal, but it is to be understood that it is not limited thereto.

In the said application, which has matured as Patent No. 2,151,578, film stabilizers, or active agents, are described by example, by physico-chemical definition, and by a definitive method, as follows:

Exemplary of the film stabilizers are the following: It is to be understood that this list is exemplary; that it is not limitative; and that it is designed to disclose illustrative examples rather than to be a catalogue of members. Any person interested in cataloging all film stabilizers from the millions of compounds known, can do so by following the definitive process which will be given after the list: catechol, resorcinol, quinol, pyrogallol, dihydroxy diphenyl, dihydroxy chlorbenzene, gallic acid, alizarin, arbutin, ruberythric acid, aloin, aesculin, apiin, glycyrrhizin, pelargonin, tannic acid, digitalin, saponin, parillin, naphthol sulfonic acid, naphthol disulfonic acid, naphthylamine disulfonic acid, amino naphthol sulfonic acid, dihydroxy naphthalene disulfonic acid, compound #8, being a condensation product of naphthalene sulfonic acid and formaldehyde, ID-1, being a reaction product of phenol sulfonic acid and formaldehyde, fastan, tanak, irgatan, sulfite cellulose, methyl cellulose, starch acetate, starch, pectin, gum arabic, gum mesquite, gum cherry, gum shiraz, gum ghatti, locust bean gum, gum karaya, gum tragacanth, carrageen, dextrin, inulin, egg albumin, blood albumin, vegetable albumin, fibrin, edestin, glycinin, alkali soluble protein (sample from corn particularly good), gliadin, casein, gelatin, bone glue, hide glue, rabbit glue, haemoglobin, polyvinyl alcohol, hexamethylene tetramine, triethanolamine, sodium phosphate, oxalic acid, potassium permanganate.

The film stabilizers are surface active substances which in aqueous solution produce an optimum differential change in surface tension with respect to concentration at concentrations of no more than about 2% and which form stable aqueous surface films in the presence of organic liquids essentially insoluble in water. Their function is physical rather than chemical and their definition is expressed of necessity in physical or physical-chemical terms. The degree of their solubility in the parting liquid is important because too great solubility in the parting liquid results in the leaching of the stabilizer out of the water film and its consequent breakdown. Consequently, solubilities of surface active substances greater than about .3% to about .5% should be avoided. Another characteristic of these surface active substances is their faculty of decreasing surface tension. The lowering of surface tension per se is probably not the cause of film stabilization, but the magnitude of the lowering, together with the concentration of the dissolved substance causing the lowering, are indications of the existence at the surface of the film of the conditions which cause film stabilization. A given solution forms the most stable films when the greatest difference exists between the concentration of the film stabilizer in the surface layer and its concentration in the solution as a whole. The film stabilizing tendency may be expressed by the ratio of the change in surface tension to the concentration at which a surface tension change is most abrupt. For example, the addition to pure water of .001% of polyvinyl alcohol produces a surface tension change of 3.60 dynes as measured on the du Nouy tensiometer, a ratio of 3.60 to .001 or 3600 to 1. A similar change of glycerol concentration in water at 10% changes the surface tension by only .5 dyne. The ratio in that instance is that of .5 to 10 or .05 to 1. On this basis polyvinyl alcohol at .001% concentration is 72,000 times as good a film stabilizer as glycerol. The film stabilizers produce a relatively great ratio of change in surface tension for increments of addition at concentrations less than about 2%, and some of the best produce excellent results at concentrations as low as .05%. The entrapment of air on the surface of the mineral as it plunges into the prewetting bath does not impair the action of the stabilized film. The stabilized films are stable at air-liquid interface and also at liquid-liquid interface, in both cases it being understood that the general conditions as hereindescribed apply. Taking a .5% solution as a standard, those surface active substances are useful film stabilizers which show by the addition of that concentration to pure water a surface tension decrease of about .5 dyne or more.

Certain compounds are not themselves film stabilizers but react with materials in the system

to produce compounds which are film stabilizers. To this class belong sodium phosphate, oxalic acid and potassium permanganate. It is within the scope of our invention to add the stabilizers originally or to produce them in the system.

A number of organic materials dissolve in water to give colloidal rather than true solution. The individual micelles are stabilized in the colloidal state because of their highly hydrated condition, and are thereafter classed as "emulsoid" or "hydrophile" colloids, as distinguished from the "suspensoid" or "hydrophobe" colloids which are stabilized by the presence of an electrical charge. The emulsoid colloids, examples of which are found in the above list, are useful as film stabilizers. Among the subclasses of emulsoid colloids are proteins and carbohydrates. Among the subclasses of proteins are the albumins, the globulins, the prolamins, the phospho-proteins, the sclero-proteins, and the chromo-proteins. Among the carbohydrates are cellulose derivatives, starches, pectin, gums, seaweed extracts. Emulsoid colloid solutions are characterized by relatively high viscosity; a property which can be used to make a rough demarcation between that class and other classes by stating that substances which have roughly five or more times the viscosity-increasing effect of sugar are included, but the true test of film stabilizing efficiency with these compounds is apparently the emulsoid colloidal nature of the compound, not viscosity or any other mere attribute.

A rough but not entirely accurate test for film stabilizers is to agitate a typical parting liquid of the type used in this invention with water in the presence of a small quantity of the substance being investigated. Many film stabilizers when so treated produce a persisting interface film which can be seen with the naked eye, and which appears to have an individual existence quite apart from the water or the organic liquid, furnishing further evidence that the properties of active agents are not merely those of wetting agents.

Another class which is shown to be effective by the illustrated members in the preceding list are the glycosides. The best compounds of this type appear to be those in which the aglucone is an unsymmetrical polyhydroxy aromatic compound. The glycosides from monohydroxy and symmetrical aglucones are of less efficiency. The principal types of glycosides are, however, actually based on the unsymmetrical and polyhydroxy type and they are all effective. Representatives of the more important classes are the phenolic type, such as arbutin, salicin, and tannic acid; the anthraquinone type, such as ruberythric acid and aloin; the coumarin type, such as aesculin; the anthoxanthin type, such as apiin and glycyrrhizin; the anthocyanin type, such as pelargonin; the digitalis type, such as digitalin; and the saponin type, such as parillin.

Since the large number of known chemical compounds and the diversity of their constitutions and attributes make a listing of the entire group of film stabilizers too wasteful in time and too expensive in money to be practical, the following definitive method has been developed as an additional means of defining the class as a whole. This method is applicable to all known substances: A number of tubes having transparent bottoms and equal diameter are filled to equal depth with solutions of dye and kerosene, the tubes being arranged so that light will travel up through the transparent bottoms through the dye solution. The tubes are arranged in the order of increasing percentages of dye. For instance, the first tube may contain 1% of an oil-soluble dye, such as oil red, the second tube, 2%, etc. A sample of coal of unknown properties is agitated gently in plain water, the agitation being controlled so that degradation of the coal will be kept at a minimum. The agitation continues for an exact period of time, such as fifteen seconds. The coal is then separated from the water and is immersed for an exact period of time, such as fifteen seconds, in an essentially water insoluble organic liquid, such as pentachlorethane, in which has been dissolved a small percentage, such as 0.1%, of the same dye which is found in the kerosene tubes. The coal is separated from the organic liquid, is vigorously sprayed with water for an exact period of time, such as twenty seconds, and is immersed in a weighed quantity of kerosene in which it is gently agitated for an exact period of time, such as fifteen seconds. The coal and the kerosene are separated; the kerosene is filtered; the coal is weighed, and a tube of the same size as the color tubes is filled to identical depth with the kerosene extract. By comparing the color of the kerosene extract with the color in the tubes there is obtained by simple mathematics an accurate statement of the liquid loss on the particular type of coal constituting the sample.

Liquid losses vary according to the type of coal. A compact, hard anthracite shows a relatively low liquid loss, whereas the friable bituminous coal which is continually presenting fresh surfaces by degradation and which is filled with fine cracks and fissures into which the liquid can penetrate, shows a relatively great loss.

In the second step of the defining process a sample of the same coal is immersed for an identical period of time in an aqueous solution of the compound, whose efficiency is to be determined, for example, in a .1% solution of starch acetate, and the foregoing procedure is otherwise identically followed. Those compounds whose presence in the second step produces a color of less intensity than the color produced in the first step are film stabilizers, and their efficiency as such is indicated with accuracy by the difference in shade. The foregoing definitive method requires only a few seconds for completion and is in all cases applicable and in all cases accurate within practical limits. The efficiency of film stabilizers differs according to the type of coal, for the reasons above set forth, according to the nature of the film stabilizer, and according to the percentage of the film stabilizer used. In some instances .05% of film stabilizer produces optimum results. In other instances 1% or even more concentrated solutions of film stabilizer are required to obtain optimum efficiency.

This definitive method also defines the characteristics of each type of coal and enables the operator to be sure that the film stabilizer he is using is the best type for the particular type of coal and to be sure that it is being used in the percentages which produce the optimum result.

Certain types of soft coal are drawn from the ground filled with minute cracks and are of highly frangible character. During the treatment of such coals according to the process of the identified case, the pieces break in the normal operation of the process, continually exposing new surfaces. Furthermore, the cracks seem to absorb quantities of parting liquid which cannot be readily removed. In such coals losses of parting

liquid of 200 ounces a ton are not infrequent where a mere preliminary washing with water, such as recommended in Moxham 1,294,519 or Nagelvoort 1,839,117, is used and the sink and float process is for that reason commercially impractical. The use of an aqueous bath containing a film stabilizer reduces the losses greatly, but still leaves them too high to be satisfactory. Different types of film stabilizer solutions produce different degrees of effect, but none are in general satisfactory with the more difficult types of coal, although some are wholly satisfactory with other types of coal.

It is an object of this invention to develop a process to reduce the losses of parting liquid on coal and other organophylic minerals and on the surfaces of their indigenous impurities, and to inhibit the adhesion of organophylic materials and organic liquids.

The objects of the invention are accomplished, generally speaking, by washing the mineral with a compound which will react with a water film stabilizer, as defined in the identified application, to form a compound which is insoluble in water, subjecting the mineral to an aqueous washing, and applying thereto a film stabilizer, as defined in the identified application. Raw coal treated in this manner and then subjected to partition in a halogenated hydrocarbon liquid may be freed of that liquid, to a degree not otherwise possible, by a simple washing in water. A particularly advantageous result is obtained if both the first and second compounds are film stabilizers. The advantages of this invention are not generally attained if the first applied of the reactants is a film stabilizer and the second is not.

It has been thought that the reaction precipitates points of anchorage upon the mineral surface to which the stabilized film may attach itself, but applicants present the herein-described facts without subscribing to any particular theory.

The following examples illustrate a particular procedure including the invention. The coal used was bituminous from the Upper Kittanning seam.

Example I

Coal was immersed for 20 seconds with agitation in a 0.05% solution of medium viscosity starch acetate, was removed and washed for 10 to 20 seconds with water from sprays, free drainage insuring removal of fine particles carried by or breaking off, the surface of the coal. The so-prepared solids were immersed for 20 seconds in a 0.05% solution of tannic acid, using moderate agitation, and were drained for 5 to 10 seconds. The coal was separated from the slate and other contaminants by flotation in a bath of pentachlorethane diluted by kerosene to a specific gravity of 1.40. The slate and heavy refuse sank to the bottom of the tank. The coal and refuse were transferred to separate washer screens, were washed with water saturated with the separating liquid, and passed through nine banks of fish-tail sprays in a period of 30 seconds.

The combined loss of parting liquid carried off on coal and refuse leaving the operation amounted to 5 to 7 ounces per ton or less. In contrast to this, it was found that the loss amounted to more than 100 ounces per ton if plain water was substituted for the solutions.

Example II

The procedure was the same as that of Example I, except that a 0.1% solution of a synthetic tanning agent (condensation product of formaldehyde and naphthalene sulfonic acid) was substituted for the starch acetate solution, and a 0.1% solution of animal glue was substituted for the tannic acid solution.

Loss of halogenated hydrocarbon liquid in this case was about 8 ounces per ton.

Example III

The procedure was the same as that of Example I, except that a 0.1% solution of phosphomolybdic acid was substituted for the first compound and a 0.1% solution of blood albumin for the second.

Loss of halogenated hydrocarbon liquid in this case was 9 to 10 ounces per ton.

In order to produce effective pre-wetting, particularly in the case of bituminous coals, a multi-stage treatment must fulfill two principal requirements: (1) the agents applied in the initial and final wetting steps must combine, either chemically or physically, to yield an insoluble product, and (2) whatever type of agent is used in the initial stage, an aqueous bath containing a film stabilizer must be used in the final stage. Optimum results have been obtained from the use of mutually reactive film stabilizers in the first and final baths. For example, tannic acid and the natural tannins precipitate any of the emulsoid colloids, and both classes are outstanding as "film stabilizers", so that combinations representing members of these groups are unusually effective. Combinations of synthetic tanning agents with various protein colloids are also highly effective. Mutually reactive emulsoid colloids are not common, but the well established reactive combination of casein and haemoglobin has been shown to be operative in this invention.

While it is preferred to use combinations comprising film stabilizers in both initial and final stages, good results have been secured when the agent used initially is not a film stabilizer, but merely a precipitant for the film stabilizer used in the final step. Thus, protein colloids may be precipitated on the solids by using heavy metal salts, complex anions and azo dyes as the first applied compound, none of which shows "active agent" properties, and such combinations may be used successively in the order precipitant/protein colloid. Similar results may be obtained with a precipitant and carbohydrate colloid, as for example iodine/starch. Another effective combination using a film stabilizer only in the final wetting stage is iron salt/tannin.

The concentrations of agent which must be used in the initial and final wetting stages will vary according to the particular combination selected. In certain cases it has been found that solutions containing as little as 0.01% agent will function satisfactorily. In other cases 0.1% or even 1.0% solutions may be required.

It will be noted that with tannin/emulsoid colloid and syntan/protein combinations a low pH is favorable, and the preferred range for such combinations is a pH of 2–4. However, good results have been obtained in neutral solutions and even at a pH as high as 10. In the case of combinations involving the precipitating effect of heavy metals or complex anions on proteins, it is important to have the pH adjusted properly in terms of the iso-electric point of the protein. That is, proteins react as acids and are precipitated by heavy metals at a pH above the iso-electric point, which is usually about 5. For precipitation with complex anions, it is necessary to have a low pH. It will thus be seen

that pH should be adjusted in each case to secure optimum reactivity, and will vary considerably depending upon the combinations selected.

The time of contact between coal and agent solution is not particularly critical, a few seconds being ample. In practical operations the rate at which coal can be transferred from one stage to the next is such that each solution will remain in contact with the coal for periods longer than are actually necessary.

The intermediate washing between wetting steps is quite important, and should be sufficient to remove the fine particles and dust from the surface of the coal. The efficiency of washing will vary depending on the type of spray and its position in relation to the coal, so that limitations cannot be set up easily. This operation must be adjusted for each installation to give the proper results.

The separation and final washing steps are essentially those disclosed in the identified Alexander, du Pont and Foulke application, and require no further comment here. That case also lists the various parting liquids suitable for sink-and-float separations. The treatment covered by this invention is effective with all members of the class.

The commercial success of the sink-and-float process in coal cleaning is dependent upon almost complete recovery of the parting liquid used. It has been shown previously that with a typical anthracite coal the loss of parting liquid can be reduced from a value upward of 50 ounces per ton for no agent treatment to as little as 5 ounces per ton by a simple pre-wetting with water containing a film stabilizer. This method has also given reasonably low losses with the harder varieties of soft coal. The more friable types of soft coal, such as that taken from the Upper Kittanning seam, are much more difficult to pre-wet effectively. Such coals show losses of 70–200 ounces per ton when no agent is used, and when treated with film-stabilized solutions by the technique developed for anthracite, the losses are still in the range of 20–50 ounces per ton.

The multi-stage wetting treatment described in this invention is the only method known by which parting liquid losses for friable soft coals can be reduced to a practical range, i. e., 5–10 ounces per ton. This is illustrated by the following data for multi-stage treatments carried out under the specified conditions, and variations on this process which depart from standard in different respects.

Upper Kittanning seam coal—1.40 gravity pentachlorethane pre-wetting treatment

	Parting liquid loss
	Ounce-tons
No agent	72
0.1% phosphomolybdic acid (not an "film stabilizer")	71
0.1% blood albumin ("film stabilizer")	38
No agent/wash/0.1% blood albumin	21
0.1% blood albumin/wash/0.1% blood albumin (no reaction)	22
0.1% blood albumin/wash/0.1% phosphomolybdic acid ("film stabilizer" first)	28
0.1% phosphomolybdic acid/wash/0.1% blood albumin ("film stabilizer" last)	9½
0.1% tannic acid/wash/0.1% blood albumin ("film stabilizer" in both stages)	6½

In some cases the coal as it comes from the mine carries a definite amount of soluble iron. Such coal will show low losses when merely given a preliminary wash and treated with tannic acid, as the iron already present serves as the precipitating agent usually applied in the initial stage. However, the iron content varies greatly even in day to day operations, so that the use of tannic acid with no more than a preliminary wash cannot be considered an adequate substitute for the complete multi-stage treatment.

Multi-stage treatments sometimes have advantages over single stage wetting methods with anthracite as well as bituminous coals, and offers possibilities in simplification of the final washing step.

Other useful combinations are illustrated by the following table:

Agent	Liquid loss
	Ounce-tons
No agent	70–80
0.1% starch/0.5% tannic acid	5.3
0.1% gum arabic/0.5% tannic acid	5.1
0.1% casein/0.5% tannic acid	5.6
0.1% haemoglobin/0.5% tannic acid	6.5
0.1% starch acetate/0.5% tannic acid	7.0
0.1% starch/0.1% quebracho ext	6.7
0.1% casein/0.1% quebracho ext	7.5
0.1% starch/0.1% myrobalan ext	6.3
0.1% blood albumin/0.1% myrobalan ext	10.7
0.1% tannic acid/01.% glue	6.0
0.05% tannic acid/0.1% blood albumin	6.4
0.1% tannic acid/0.1% starch acetate	10.1
0.1% Leukanol/0.01% glue	8.0
0.1% sulfite cellulose/0.1% blood albumin	7.8

Certain of the emulsoid colloids are mutually reactive, e. g. casein/haemoglobin, gelatin/gum arabic, and starch/albumin. The latter two pairs react only under delicately adjusted pH conditions, and it has not been practical to secure positive effects in a wet/wash/wet procedure with those combinations. Casein and haemoglobin show definite precipitation under ordinary conditions, however, and liquid losses of 8.0 ounces per ton have been secured with that combination. The excellent results obtained with casein/haemoglobin, colloids/tannins, and protein colloids/syntans establishes the general applicability in multi-stage wetting treatments of any pair of film stabilizers known to precipitate each other.

When wetting agents are used in both stages, the better agent should be used in the final step for optimum results. This is illustrated by the following data:

Wetting treatment	Liquid loss
	Ounce-tons
No agent	70–80
Water/wash/0.1% blood albumin (good)	21.0
Water/wash/0.1% sulfite cellulose (fair)	53.0
0.1% blood albumin/wash/0.1% sulfite cellulose	17.4
0.1% sulfite cellulose/wash/0.1% blood albumin	7.8

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that we do not limit ourselves to the specific embodiments thereof except as defined in the appended claims.

We claim:

1. In the process of separating coal from indigenous impurities by the intermediation of a water-insoluble organic parting liquid the process which comprises applying to coal-containing solids a compound which will react with a film stabilizer to form a water insoluble product, washing the solids with water, and applying to the solids a film stabilizer which will react with the said compound to produce a water-insoluble precipitate.

2. In the process of separating mineral from indigenous impurities by the intermediation of a

water-insoluble organic parting liquid the process which comprises applying to mineral containing mass a compound which will react with a film stabilizer to form a water insoluble product, washing the solids with water, and applying to the solids a film stabilizer which will react with the said compound to produce a water-insoluble precipitate.

3. In the process of mineral beneficiation by the intermediation of a water-insoluble organic parting liquid, the process which comprises applying to the mineral-containing mass an aqueous solution of a film stabilizer, washing the mineral containing mass with water and applying thereto an aqueous solution of a different film stabilizer which will react with the first film stabilizer to produce a compound insoluble in water.

4. In the process of mineral beneficiation by the intermediation of a water-insoluble organic parting liquid, the process which comprises applying to the mineral containing mass an aqueous solution of tannic acid, washing the mineral containing mass with water and applying thereto an aqueous solution of starch acetate.

5. In the process of mineral beneficiation which involves the intermediation of a water-insoluble organic parting liquid, the steps which comprise applying to the mineral an aqueous solution of a compound which will react with a film stabilizer to form a water-insoluble precipitate and thereafter applying an aqueous solution of a film stabilizer which will react with the said compound to form a water-insoluble precipitate.

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