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PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Improvements in or relating to the Treatment of Sulphur Pitch and Resins

We, ELLIOTT ASSOCIATED DEVELOPMENTS LIMITED, a British Company of 22, Bishopsgate, London, E.C.2, do hereby declare this invention for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to the pelletisation of sulphur, pitch and resins. More particularly, it is concerned with the conversion of these materials into pellets that can be handled readily and conveniently.

A primary object of the invention is to provide a pelletising process that will produce, in a comparatively simple apparatus, hard moisture-free pellets suitable for transportation by, for example, pneumatic handling equipment.

One advantageous pelletising technique, applicable specifically to sulphur, is described in our patent application Serial No. 1136901. The sulphur to be pelletised is delivered, in the molten condition, into a body of water at substantially atmospheric pressure, and means are provided to keep the resulting globules or droplets moving in the water and to prevent them massing or piling up together until in the course of solidifying they have reached a condition, at least externally, in which they do not adhere to one another.

The present invention comprises, in a process for pelletising sulphur, pitch or resins by the solidification of molten globules thereof in water, the addition of an additive to the water which has the property of inhibiting coalescence or binding together of the solidifying globules or soft pellets or sticking thereof to the surfaces of the apparatus employed.

Polymers of the class known as silicone fluids are particularly useful. It is, of course, necessary to employ a silicone compound that is stable in the pelletising environment. Also, results in any particular case vary with the viscosity or molecule size of the silicone. It is possible to ascertain the optimum viscosity range by simple experiment.

[Price 4s. 6d.]

Methods of carrying the invention into practice will now be described by way of example and with reference to the accompanying drawings, in which:—

Figure 1 is a diagrammatic elevation of a sulphur pelletising plant, and

Figure 2 illustrates a possible modification of that plant.

Referring to Figure 1 of the drawings, a molten sulphur feed, for example at about 130—140°C. at which temperature the sulphur becomes quite free flowing, is delivered to a molten sulphur reservoir 11 at the top of a pelletising vessel 12 of short columnar form. The floor of the reservoir 11 is formed by a plate 13 in which are fitted a large number of nozzles 14, say 1½ to 2 mms. in diameter, which deliver the molten sulphur downwardly beneath the plate 13 in separate streams. Some distance beneath the nozzle plate 13 but still fairly near the top of the vessel 12 is an impeller disc 15 which is rotated by a vertical shaft 16. The vessel 12 is filled with water to a level well above the disc 15 but a few inches, say 2" to 4", below the nozzle plate 13, and the disc 15 creates a vortex or swirl in the body of water.

The molten sulphur streams from the nozzles 14 break up into globules or droplets immediately below the water level after entry and are caught up in the swirl or vortex created by the rotation of the impeller disc 15 and caused to follow a path which is more or less spiral as they drop through the vessel. At its lower end the vessel 12, which may be, say, about three feet high, has a coned bottom 18 in which the sulphur bodies, now solidified into pellets, collect and from where they are withdrawn through a trap 17. A screen 19 removes the water from the pellets and delivers them in a substantially dry condition, while the extracted water is returned to the vessel 12 via a line 20.

The vessel 12 is operated at atmospheric pressure. The water will, of course, heat up due to the molten sulphur entering it and

therefore circulation is maintained to remove the hotter water at the top and replenish lower down with cooler water. Some of the entering water can be introduced by way of tangential entries 21 at various places in the side wall of the vessel 12 so as to further promote the swirling in the vessel. A heater may be provided around the upper portion of the vessel for controlling the water temperature in this region.

The speed of rotation of the impeller disc should be high enough to prevent any deposit of sulphur on the impeller. The strong, vortex water wall directly over the impeller disc and the radial pressure discharge at the periphery of the disc has the effect of breaking up the sulphur droplets to a smaller size whereas droplets falling outside the main vortex near the vessel wall will not be subjected to such a strong action and therefore remain larger. It is, in general, desirable to obtain a product in which the pellets vary in size, as close packing then occurs to give a high bulk density. It is, however, undesirable that sulphur droplets should be permitted to fall into the comparatively calm centre or "eye" of the vortex.

To prevent a funnel of air in the vortex from interfering with the satisfactory production of pellets, a barrier element can be mounted above the impeller to check the downward extent of this funnel. The carrier element may be mounted on the impeller shaft to rotate therewith, as at 22, or it may be a fixed element carried, for example, from the wall of the vessel. The interior of the pellets produced appears to be rhombic crystal sulphur while the crust is amorphous. The amorphous crust is hard, smooth and rounded and makes the pellets particularly suitable for handling by, for example, pneumatic means.

The impeller disc can be dished or flat. And various configurations of blades may be employed thereon. The exact design of the impeller, and its speed, depth of immersion and clearance from the vessel side wall are chosen to suit the circumstances of each particular plant and the nature of the product desired. By raising and lowering the impeller it is possible to vary the size of the pellets produced. Especially good control of pellet size can be achieved by the use of a skirt 23 (Figure 2) around the impeller which has four internal deflector humps 24 of smooth arcuate form disposed equidistantly around its periphery. To form these humps the skirt 23 has four part-cylindrical concavities 25 at 90° intervals.

The skirt 23 with its concavities should preferably extend from above the water level in the vessel to some distance below the level at which the impeller normally operates. It is convenient to use the four passages formed between the humps 24 and the wall of the vessel 12 as off-takes for water flowing upwards in the vessel and there may, if desired, be mesh or gauze material, e.g. 60 mesh

(Tyler) gauze, across the bottom ends of these passages to prevent carrying of sulphur pellets into the overflow. At their upper ends the four passages may communicate with an annular overflow channel.

If the impeller is progressively lowered from within the skirt to a level below it the pellet size will increase, and therefore we have a simple and inexpensive way of making a pelletising vessel that can be rapidly adjusted, without dismantling or the addition or removal of parts, to produce pellets of varying sizes according to the purpose for which they are required.

Since the pellets constituting the product are required for use in a dry state, it is advantageous if they leave the vessel 12 at a reasonably elevated temperature to assist natural drying. We have discovered that certain additives to the water in the vessel are especially valuable in this connection. In particular, fluid silicone polymers may be used to advantage.

There are many silicone additives that give beneficial results, but in general those of higher viscosity are preferred, such as F111/30,000 of Imperial Chemical Industries Limited with a viscosity of 3,000 centistokes at 25°C. This is a straight chain dimethyl type silicone with trimethyl silyl end-stopping of the chains. The lower viscosity silicones of this type seem to be less efficient, and a viscosity range of 30,000 to 100,000 centistokes is preferred. The pure silicone is diluted in a solvent, for example benzene or toluene, to enable it to be dispersed in the water body to the best extent.

It will be understood that liquid silicones with sufficient chain length and stability are employed, such as the dimethyl silicones and phenyl substituted polysiloxanes. It is necessary to choose a silicone fluid which is stable in the pelletising environment. A 5% solution (by volume) in benzene or toluene of a dimethyl silicone with trimethyl silyl end-stopping is particularly satisfactory.

As to the amount to be added this can readily be determined for each silicone by simple experiment; too little does not give the required result and too much either shows no significant improvement over the correct amount or in some cases results in the sulphur joining up into thread or string-like formations. A few parts per million (by volume) of the additive solution is ordinarily all that is required, for example 10 parts per million.

Other silicones, especially the stable methyl alkyl non-reactive kinds, can be employed. Phenyl methyl silicones give good results. Silicones with chlorophenyl and fluorophenyl groupings, and silicones with the chains end-stopped by dimethyl hydroxy groupings, may be employed if stable in the presence of the substance being pelletised. The more reactive types of silicones, such as those having cyano, amino or vinyl groups, or sulphur substituted alkyl groups, must be tested

with care as they are less likely to be stable in the pelletising environment in any particular case.

The additive apparently promotes the dispersion of the molten sulphur as globules, appears to stimulate hardening of the solidifying globules in the water and substantially counteracts any tendency the solidifying globules or still hot soft pellets may have to coalesce or bind together or to stick to the walls or bottom of the vessel or other surfaces of the apparatus.

Before the globules have travelled down any substantial distance through the water it is possible to collect them while they are still fairly soft and they will not stick together or to the walls of the collector. They can, in appropriate cases, be collected while still at a temperature as high as 56°C. This means that the temperature of the water where the sulphur stream is entering may be much nearer that of the sulphur itself, say 80 to 85°C, thus reducing thermal shock, without increasing the amount of cooling equipment needed. The temperature of the water entering at the bottom of the column will then be about 50°C.

Of course it is not necessary to remove the pellets at elevated temperature. If the pelletising plant is arranged to cool down the pellets to near ambient temperature they will be quite hard and resilient when collected and ready almost immediately for mechanical handling; they will harden still further and lose their resilience on storing.

Certain previous proposals for the pelletising of sulphur have resulted in the formation of pellets with hollow centres or a weakening "tunnel" hole therein due to free vertical fall of the droplets in water. The present technique helps to reduce the size and change the shape of this hole. Under favourable circumstances the hole can be reduced to a mere dent.

While silicones are good additives, certain other polymeric materials have been found effective, particularly certain water soluble compounds. Thus polyethylene and polypropylene oxides, polyacrylamides and polysulphites are effective to varying degrees. These materials have a limited temperature range of use but this can be raised if they are employed in conjunction with silicones. Particularly good results have been achieved with sulpho succinate compounds, for example cetyl stearyl sulpho succinate.

With regard to the plant, it is beneficial in certain cases to slant the sulphur injection nozzles but the amount and whether it is with or against the flow depends on the particular additive used. Consequently, it may be advantageous to fit swivel nozzles to allow for use of different additives.

A little pressure will ordinarily be desired to feed the sulphur through the nozzles, say 1 p.s.i.g. for 2 mm size nozzles.

Many modifications are possible without departing from the scope of the invention. Other

forms of stirrer are possible, and mechanical stirring can be reduced or in some cases dispensed with if the vortex or swirl is substantially reproduced by means of tangential water jets disposed at intervals around, and up the height, of the vessel.

The method and apparatus described enables sulphur pellets to be produced with a moisture content of less than 1% by weight, which we believe has not been possible previously because of moisture locked inside the pellets. Test results on samples of produce obtained gave moisture contents, after drying, of the order of 0.02% by weight. Also the pellets are hard and tough and well suited to pneumatic handling techniques when appropriately sized, particularly in diameters of about $\frac{1}{8}$ inch down.

Although the practical application of the invention has been described in the context of sulphur pelletising, we have found that the additives disclosed are also of benefit in the case of pelletising pitch and resins, which likewise are treated by causing molten globules to solidify in a body of cooling water.

Attention is directed to the aforementioned patent application No. 38096/64 (Serial No. 1136901), the complete specification of which describes and claims certain of the subject matter also contained in this specification.

WHAT WE CLAIM IS:—

1. In a process for pelletising sulphur, pitch or resins by the solidification of molten globules thereof in water, the addition of an additive to the water which has the property of inhibiting coalescence or binding together of the solidifying globules or soft pellets or sticking thereof to the surfaces of the apparatus employed.

2. In a process for pelletising sulphur, pitch or resins by the solidification of molten globules thereof in water, the addition of an additive to the water comprising a silicone fluid stable in the pelletising environment.

3. In a process for pelletising sulphur by the solidification of molten globules thereof in water, the addition of an additive to the water comprising a dimethyl or phenyl methyl silicone fluid.

4. A process according to claim 3, wherein the silicone is made up as a solution in a solvent.

5. A process according to claim 4, wherein the silicone is made up as a 5% solution (by volume) in the solvent.

6. A process according to claim 5, wherein the solvent is benzene or toluene.

7. A process according to claim 4, or claim 5, or claim 6 wherein the additive solution is added in the quantity of substantially ten parts per million, by volume.

8. A process according to any one of claims 2 to 7, wherein the viscosity of the silicone fluid is in the range 30,000 to 100,000 centistokes.



with care as they are less likely to be stable in the pelletising environment in any particular case.

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20 is entering may be much nearer that of the sulphur itself, say 80 to 85°C, thus reducing thermal shock, without increasing the amount of cooling equipment needed. The temperature of the water entering at the bottom of the column will then be about 50°C.

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55 certain cases to slant the sulphur injection nozzles but the amount and whether it is with or against the flow depends on the particular additive used. Consequently, it may be advantageous to fit swivel nozzles to allow for use
60 of different additives.

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2. In a process for pelletising sulphur, pitch or resins by the solidification of molten globules thereof in water, the addition of an additive to the water comprising a silicone fluid stable in the pelletising environment.

3. In a process for pelletising sulphur by the solidification of molten globules thereof in water, the addition of an additive to the water comprising a dimethyl or phenyl methyl silicone fluid.

4. A process according to claim 3, wherein the silicone is made up as a solution in a solvent.

5. A process according to claim 4, wherein the silicone is made up as a 5% solution (by volume) in the solvent.

6. A process according to claim 5, wherein the solvent is benzene or toluene.

7. A process according to claim 4, or claim 5, or claim 6 wherein the additive solution is added in the quantity of substantially ten parts per million, by volume.

8. A process according to any one of claims 2 to 7, wherein the viscosity of the silicone fluid is in the range 30,000 to 100,00 centistokes.

9. In a process for pelletising sulphur by the solidification of molten globules thereof in water, the addition of an additive to the water consisting of a 5% solution (by volume) of a silicone fluid in benzene or toluene, the silicone fluid being a dimethyl silicone with trimethyl silyl end-stopping of the silicone chain and a viscosity of substantially 30,000 centistokes.
10. A process according to claim 1, wherein the additive is a sulpho succinate.
11. A process according to claim 10, wherein the additive is cetyl stearyl sulpho succinate.
12. A process according to claim 1, wherein the additive is polyethylene oxide, polypropylene oxide, a polacrylamide or a polysulphite.

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