

PATENT SPECIFICATION

1,136,901

DRAWINGS ATTACHED.

Inventor:—HERBERT JAMES ELLIOTT.

Date of filing Complete Specification (under Section 3(3) of the Patents Act, 1949): 29 Oct., 1965.

Application Date: 17 Sept., 1964. No. 30896/64.

Application Date: 1 Dec., 1964. No. 48828/64.

Application Date: 12 Feb., 1965. No. 6288/65.

Application Date: 9 April, 1965. No. 15294/65.

Complete Specification Published: 18 Dec., 1968.

© Crown Copyright 1968.



1,136,901

Index at Acceptance:—C1 AK9B; B1 C(1, 4, 5, 10, 19A2, 19F4D).

Int. Cl.:—C 01 b 17/00.

COMPLETE SPECIFICATION.

Improvements in or relating to the Treatment of Sulphur.

We, ELLIOTT ASSOCIATED DEVELOPMENTS LIMITED, a British Company, of 22 Bishopsgate, London, E.C.2, do hereby declare the 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 treatment of sulphur. More particularly, it is concerned with the production of sulphur pellets that can be handled much more readily and conveniently than molten or block sulphur.

A primary object of the invention is to provide a process for pelletising sulphur that is simple and cheap and which gives externally hard pellets suitable for transportation by, for example, pneumatic handling equipment.

According to the present invention, sulphur is pelletised by being 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 of sulphur 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 to more than a negligible extent.

Previous proposals have been made for pelletising sulphur an essential feature of which has been the treatment of the sulphur in hot water under pressure. Since the boiling point of water at atmospheric pressure is below the melting point of sulphur, a pressure above atmospheric has been thought necessary to enable the melting point of sulphur to be reached. By contrast, the technique of this invention affords a pro-

cess for pelletising sulphur that is simpler and cheaper than the processes previously proposed, especially in that it does not require operation under superatmospheric pressure.

Another feature of some previous proposals has been the provision of a tall tower, say 40 feet high, through which the droplets of molten feed material could fall while solidifying into pellets. Such a tall tower is a costly piece of equipment to install and maintain. According to a preferred feature of the present invention, a sufficiently strong vortex or swirl is induced or created in the body of water in which the pelletisation takes place. This, together with the fact that colder water can be used, enables pellets to be obtained without the need for a tall tower or pressurised cooling column.

We have also found that a still further improvement is obtained if one or more of a certain class of surface active agents are added to the water. In the preferred method the added agents are silicones. An important result of using such agents is that the solidifying globules can be allowed to contact each other at a higher temperature with negligible risk of the pellets adhering to one another. As a consequence there is a saving in equipment, in particular plant for drying the product.

The invention also includes apparatus for carrying out the above method and the product so obtained.

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

[Price 4s. 6d.]

SPECIFICATION AMENDED - SEE ATTACHED SLIP

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 the 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 barrier 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 upwardly in the vessel and there may, if desired, be mesh or gauze material 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.

5 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 30,000 centistokes at 25°C, if operation at the more elevated
10 temperatures is required. The lower viscosity silicones tend to lose their efficacy with rise in temperature, and a viscosity range of 30,000 to 100,000 centistokes is preferred. Many silicones require dilution in a solvent,
15 for example benzene, toluene or xylene, before they will disperse in the water body to the best extent.

It will be understood that liquid silicones with sufficient chain length and heat stability
20 are employed, such as dimethyl silicones and phenyl substituted polysiloxanes. It is necessary to choose a silicone fluid which does not react chemically with the material being pelletised.

25 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 of string-like
30 formations. A few parts per million of water is ordinarily all that is required, for example 10 parts per million.

35 The additive promotes the dispersion of the molten sulphur as globules, appears to stimulate heat loss from the globules to the water and substantially counteracts any tendency the solidifying globules may have
40 to stick together or to the walls or bottom of the vessel.

Before the globules have travelled down any substantial distance through the water it is possible to collect them while they are
45 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
50 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
55 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
60 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.
65 Furthermore, the vortex or swirling action

still has the substantial advantage of producing pellets without significant perforations, by creating a kneading or rolling action on the pellets, even if by reason of the additive it is not necessary for the purpose
70 of preventing the solidifying pellets from sticking together or to the vessel.

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; in particular, the motion of the vortex has this desirable
75 effect. Under favourable circumstances the hole can be reduced to a mere dent.

Other specific silicones that have been found effective, especially at the lower temperatures, are Silcolapse (Registered Trade
85 Mark) 437 (diluted to 10% by volume before use), others in the F111 series (Imperial Chemical Industries Limited), MS 510, MS 550 and MS Antifoam emulsions RD and FG (diluted to 10% by volume) (Midland
90 Silicones Limited). Some require to be used at rather higher concentration (say 12 drops per gallon or more).

While silicones are the preferred additives, certain other polymeric materials have been
95 found effective, particularly water soluble compounds. Thus polyethylene and polypropylene oxide compounds, polyacrylamides and polysulphites are effective to varying degrees. These materials have a limited
100 temperature range of use but this can be raised if they are employed in conjunction with silicones.

With regard to the plant, it is beneficial in certain cases to slant the sulphur injection
105 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.
110

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

Many modifications are possible without departing from the scope of the invention.
115 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
120 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
125 the pellets. Test results on samples of product obtained gave moisture contents, after drying, of the order of 0.02% by weight. Also the pellets are hard and tough and well
130

suited to pneumatic handling techniques when appropriately sized, particularly in diameters of about $\frac{1}{8}$ inch down.

WHAT WE CLAIM IS:—

- 5 1. A method of pelletising sulphur, wherein the sulphur is delivered, in a molten condition, into a body of water at substantially atmospheric pressure, and means are provided to keep the resulting globules or
- 10 droplets of sulphur 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
- 15 to more than a negligible extent.
2. A method according to claim 1, wherein a vortex or swirl is created in the body of water in which the pelletisation takes place.
- 20 3. A method according to claim 2, wherein the vortex or swirl is created by means of a rotary stirrer or impeller.
4. A method according to claim 2 or claim 3, wherein the vortex or swirl is created by tangential water jets.
- 25 5. A method according to claim 2, wherein the vortex or swirl is created in the upper region of the body of water by means of a rotary impeller and in the lower region
- 30 by tangential water jets.
6. A method according to any one of the preceding claims wherein the molten sulphur is delivered downwardly from a reservoir to the body of water in separate
- 35 but continuous streams through a large number of nozzles.
7. A method according to any one of the preceding claims, wherein a polymeric surface active agent is added to the body
- 40 of water.
8. A method according to claim 7, wherein the polymeric surface active agent is a water-soluble polymer.
9. A method according to claim 7, wherein the polymeric surface active agent
- 45 is a silicone fluid.
10. A method according to claim 9, wherein the silicon has a viscosity of substantially 30,000 centistokes.
- 50 11. Apparatus when used for performing the method of any of claims 1 to 10, comprising a column designed to operate at atmospheric pressure and contain a body of water, a reservoir at the head of the column

for the material to be pelletised in molten condition, a plurality of nozzles to deliver the molten material downwardly from the reservoir into the column below in separate and continuous streams, means for creating a vortex or swirl in the water in the column, and a trap for removal of pellets at the bottom of the column.

12. Apparatus according to claim 11, wherein the means for creating a swirl comprises a rotary impeller.

13. Apparatus according to claim 11 or claim 12, including a water inlet at or near the bottom of the column and a water outlet at or near the top.

14. Apparatus according to claim 11 or claim 12 or claim 13, wherein the means for creating a swirl comprises tangential water jets.

15. Apparatus according to claim 12, wherein a barrier plate is mounted above the impeller.

16. Apparatus according to claim 12, or claim 15, wherein means is provided in the column around the region containing the impeller to deflect back inwardly toward the impeller the material impelled outwardly thereby.

17. Apparatus according to claim 16, wherein the deflector means comprises a sleeve disposed coaxially within the column and having at its periphery one or more inwardly-projecting humps.

18. A method of pelletising sulphur according to claim 1, substantially as described herein.

19. Pelletising apparatus substantially as described herein with reference to Figure 1 of the accompanying drawings, or as modified in Figure 2.

20. Pellets of sulphur made by the method according to any of claims 1 to 10 and 18, or in an apparatus according to any of claims 11 to 17 and 19.

21. Sulphur pellets containing less than 1% by weight of moisture.

22. Sulphur pellets containing substantially 0.02% by weight of moisture.

For the Applicants:
LLOYD WISE, BOULY & HAIG,
Chartered Patent Agents,
Norman House,
105—109 Strand,
London, W.C.2.

sited to pneumatic handling techniques when appropriately sized, particularly in diameters of about $\frac{1}{8}$ inch down.

WHAT WE CLAIM IS:—

5 1. A method of pelletising sulphur, wherein the sulphur is delivered, in a molten condition, into a body of water at substantially atmospheric pressure, and means are provided to keep the resulting globules or
10 droplets of sulphur 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
15 to more than a negligible extent.

2. A method according to claim 1, wherein a vortex or swirl is created in the body of water in which the pelletisation takes place.

20 3. A method according to claim 2, wherein the vortex or swirl is created by means of a rotary stirrer or impeller.

4. A method according to claim 2 or claim 3, wherein the vortex or swirl is created by tangential water jets.

25 5. A method according to claim 2, wherein the vortex or swirl is created in the upper region of the body of water by means of a rotary impeller and in the lower region
30 by tangential water jets.

6. A method according to any one of the preceding claims wherein the molten sulphur is delivered downwardly from a reservoir to the body of water in separate
35 but continuous streams through a large number of nozzles.

7. A method according to any one of the preceding claims, wherein a polymeric surface active agent is added to the body
40 of water.

8. A method according to claim 7, wherein the polymeric surface active agent is a water-soluble polymer.

9. A method according to claim 7, wherein the polymeric surface active agent
45 is a silicone fluid.

10. A method according to claim 9, wherein the silicon has a viscosity of substantially 30,000 centistokes.

50 11. Apparatus when used for performing the method of any of claims 1 to 10, comprising a column designed to operate at atmospheric pressure and contain a body of water, a reservoir at the head of the column

for the material to be pelletised in molten condition, a plurality of nozzles to deliver the molten material downwardly from the reservoir into the column below in separate and continuous streams, means for creating
55 a vortex or swirl in the water in the column, and a trap for removal of pellets at the bottom of the column.

12. Apparatus according to claim 11, wherein the means for creating a swirl comprises a rotary impeller.

13. Apparatus according to claim 11 or claim 12, including a water inlet at or near the bottom of the column and a water outlet at or near the top.

14. Apparatus according to claim 11 or claim 12 or claim 13, wherein the means for creating a swirl comprises tangential water jets.

15. Apparatus according to claim 12, wherein a barrier plate is mounted above the
75 impeller.

16. Apparatus according to claim 12, or claim 15, wherein means is provided in the column around the region containing the impeller to deflect back inwardly toward the impeller the material impelled outwardly
80 thereby.

17. Apparatus according to claim 16, wherein the deflector means comprises a sleeve disposed coaxially within the column and having at its periphery one or more inwardly-projecting humps.

18. A method of pelletising sulphur according to claim 1, substantially as described
90 herein.

19. Pelletising apparatus substantially as described herein with reference to Figure 1 of the accompanying drawings, or as modified in Figure 2.

20. Pellets of sulphur made by the method according to any of claims 1 to 10 and 18, or in an apparatus according to any of claims 11 to 17 and 19.

21. Sulphur pellets containing less than 1% by weight of moisture.

22. Sulphur pellets containing substantially 0.02% by weight of moisture.

For the Applicants:
LLOYD WISE, BOULY & HAIG,
Chartered Patent Agents,
Norman House,
105—109 Strand,
London, W.C.2.

