The present invention is directed to a method for recovering from a vapor product stream, a product which is normally solid and is capable of undergoing sublimation. A typical product of this type is phthalic anhydride, produced by the oxidation of naphthalene or ortho-xylene.

According to the present invention, a sublimable constituent is removed from a vaporous mixture by passing the mixture through a cooling zone in which is maintained a suspension of the sublimable material in solid form and in a state of turbulent motion; preferably the vaporous mixture is passed upwardly through the cooling zone at a velocity sufficient to maintain the finely divided solid sublimable constituent in the desired state of suspension. In one type of operation the velocity of flow of the vaporous mixture is such as to carry the finely divided solid suspended in it through the cooling zone at a lesser rate than the vaporous mixture itself. In this type of operation all of the solid material is carried out of the top of the cooling zone. In another type of operation the velocity of the vaporous mixture is such as to carry the solid sublimable material only partly through the cooling zone where it is concentrated in what may be termed a dense phase from which the solid material drops out by gravity and is withdrawn from the bottom of the zone while the residual vapor passes out overhead.

The presence of the solid sublimable material in the cooling zone serves several purposes: first, it provides nuclei for the deposition of sublimable material from the vapor state. Second, it serves to scour the cooling surfaces, keeping them clear of incrustations. Third, it improves the heat transfer between the cooling surfaces and the vapors. In this connection in the preferred mode of operation, according to the present invention, the solid sublimable material is precooled. In its precooled state it has the ability of taking up considerable quantities of heat from the vaporous mixture. It therefore contributes directly to the condensation of the sublimable constituent in the vaporous mixture.

In the condensation of a sublimable substance from a vapor mixture, there is frequently formed a fog due to overcooling of the vapor. This fog contains the solid in a form which separates from the vapor with considerable difficulty. The formation of such fogs is inhibited or repressed by the presence of the suspended particles in a state of turbulent flow in accordance with the present invention.

The nature and objects of the present invention may be more clearly understood from the following detailed description of the accompanying drawing, in which:

Figure 1 is a front elevation partly in section, of one type of apparatus suitable for the practice of the present invention;

Figure 2 is a similar view of a modified form of apparatus;

Figure 3 is a similar view of a condensation chamber of the type shown in Figure 1; and

Figure 4 is a transverse section along the line A—A of Figure 3.

Referring to the drawing in detail, numeral 1 designates a vessel or shell enclosing the condensation zone. Inside this vessel is mounted a bundle of tubes 2 having their ends mounted in webs 3 having inclined surfaces. The webs 3 are welded or otherwise connected to the vessel 1 so as to form a fluid-tight zone around the tubes 2. An inlet 4 for cooling fluid into the zone is provided near the bottom thereof, while an outlet 5 for this fluid is provided near the top of said zone. At the bottom of the vessel is a line 6 for the introduction of a vaporous mixture containing a sublimable material. At the upper end of the vessel is an outlet 7 for vaporous residue carrying the sublimable material in solid form. This line discharges into a separator 8 in the upper portion of which is mounted a cyclone separator 9.

The residual vapors leave the settler 8 through the line 10 while separated solids fall to the bottom of the settler, some entering the settler through the downpipe 11 of the cyclone separator. The lower portion of the settler is divided into two hoppers 12 and 13, between which there is a partition 14 which may be swung into any desired position to regulate the amount of solid material which falls into the respective hoppers. Hopper 13 discharges into a cooling zone 15 provided with a cooling coil 16. If desired, the vaporous outlet from line 10 can be fed through this cooling coil. The lower end of the hopper 12 is provided with a slide valve or other suitable valve 17 for the withdrawal of solid product from the system.

The solid sublimable material passes through the cooling zone 15 and collects at the bottom thereof, from which it is fed by means of a star wheel 18 or other suitable feeding device into the inlet line 6. In order to avoid packing of the solids in the cooling zone 15, it is preferred to provide suitable vertical and circumferentially spaced nozzles 19 on this chamber through which may be injected a fluidizing gas. This expedient serves to maintain the solid in the cooling zone in
a fluidized condition in which it acts as a liquid having a head which exerts a propelling force in the system. For this purpose the residual vapors leaving through line 10, or part thereof, may be supplied to the injection nozzles 19 to serve as the fluidizing medium in zone 15. Also the star wheel or similar feeding mechanism may be dispensed with and sufficient head of fluidized solids maintained in the vessel 1 to cause the fluidized solid to feed into inlet line 6 at any desired rate adjusted with respect to the feed rate of the vapors in line 6 to maintain the desired density of solids in the condenser 1.

In the case of the recovery of phthalic anhydride, for example, from a vaporous reaction mixture containing it, as for example, the reaction mixture resulting from the vapor phase oxidation of naphthalene, the vaporous product is preliminarily cooled by passage through cooling coils to a temperature of about 300° C, so that when the solubilic anhydride is introduced into the mixture it will not readily sublime. In this operation the cooling coil 16 may be dispensed with or may be used to circulate cold water if desired. It is sufficient, however, that the solid phthalic anhydride be at a temperature of not greater than 200° C or an equivalent temperature. The vaporous mixture containing the solid phthalic anhydride is fed into the bottom of the vessel 1 through the tube bundle 2 around which may be circulated water. The velocity of the vapors is so maintained that it carries the solid phthalic anhydride through the vessel 1 at a lower rate than it travels itself, whereby the solid phthalic anhydride has a longer residence time in the tube bundle than the vaporous material. The mixture discharges into settler 9 where the solid phthalic anhydride falls to the bottom, passing into discharge hopper 12 and the remainder going into the return hopper 13. It will be understood that instead of feeding the solid phthalic anhydride to the line 6 it may be blown directly into the bottom of vessel 1 near the inlet to the tube bundle to eliminate the possibility of any sublimation of the recycled phthalic anhydride.

When the system is in operation, the amount of solid added to the condenser should be sufficient with relation to the velocity of the vapors through the condenser to maintain at least about 5% per cubic foot of vapor space. This requires a fairly low velocity of vapors through the condenser, as for example, from 3 to 7 feet per second. With a velocity in this range, the solids are added to vapor stream or the condenser at a rate of from about 10 to 100 per minute per square foot of cross-section of vapor space of condenser.

In Figure 2 there is illustrated what may be referred to as the downflow type of operation. In this operation the vessel 19 is provided with a cooling coil 20 and at its upper end with a cyclone separator 21 having a vapor exhaust line 22 and a downpipe 23. The downpipe discharges into the open mouth of a funnel 24 arranged below the cooling coil, the spout of which is connected to a pipe 25 which enters through the lower end of the vessel and through which the vaporous mixture containing the sublimable mixture is introduced. At its lowermost portion the vessel 19 is provided with a drawoff 26 for solids controlled by a valve 27. Above this drawoff is a second drawoff 28 which discharges into a cooling chamber 29 which has its bottom in the shape of a hopper 30 in which is arranged a worm 31 for feeding the solid material from the vessel 29 into the inlet tube 25. In this operation the vaporous mixture carrying the solid sublimable material is fed into the vessel at a velocity such that the solid material is carried only about the top of the cooling coil, forming around the coil a condition which may be referred to as a dense phase. Actually the cooling zone 15 to cause the fluidized solid to feed into inlet line 6 at any desired rate adjusted with respect to the feed rate of the vapors in line 6 to maintain the desired density of solids in the condenser 1.

In the case of the recovery of phthalic anhydride, for example, from a vaporous reaction mixture containing it, as for example, the reaction mixture resulting from the vapor phase oxidation of naphthalene, the vaporous product is preliminarily cooled by passage through cooling coils to a temperature of about 300° C, so that when the solubilic anhydride is introduced into the mixture it will not readily sublime. In this operation the cooling coil 16 may be dispensed with or may be used to circulate cold water if desired. It is sufficient, however, that the solid phthalic anhydride be at a temperature of not greater than 200° C or an equivalent temperature. The vaporous mixture containing the solid phthalic anhydride is fed into the bottom of the vessel 1 through the tube bundle 2 around which may be circulated water. The velocity of the vapors is so maintained that it carries the solid phthalic anhydride through the vessel 1 at a lower rate than it travels itself, whereby the solid phthalic anhydride has a longer residence time in the tube bundle than the vaporous material. The mixture discharges into settler 9 where the solid phthalic anhydride falls to the bottom, passing into discharge hopper 12 and the remainder going into the return hopper 13. It will be understood that instead of feeding the solid phthalic anhydride to the line 6 it may be blown directly into the bottom of vessel 1 near the inlet to the tube bundle to eliminate the possibility of any sublimation of the recycled phthalic anhydride.

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In this modification the solid is added to the condenser at a rate so adjusted to the vapor flow as to maintain in the condenser at least about 10# per cu. ft. of vapor space. This requires a relatively low vapor velocity, as for example, from about 5 to about 5 feet per second through the condenser. With such velocities the solid is added to the condenser at a rate between about 10# and 500# per minute per square foot of cross-section of vapor space of condenser.

In Figure 3 is shown a type of tube bundle that is particularly useful for the practice of the present invention. Here again, the shell is indicated by numeral 1 and the individual tubes by numeral 2, while the web by which the tube bundle is connected to the shell is indicated by numeral 3.

As will be seen, each tube has both ends flared outwardly, as at 4, with the outer edge having a polygonal configuration 5. In this case, hexagonal. These outer edges of the tubes are connected together by welding or brazing.

As can be seen, this construction eliminates all transverse surfaces at the ends of the tube bundle, presenting only sharp edges to the material entering the bundle. In addition, the entrance to the individual tubes is streamlined so that a minimum of resistance is offered to any fluid passing through the bundle.

In the foregoing discussion emphasis has been placed on the inclusion, in a vaporous product containing a sublimable constituent being fed to a condensing zone, of some of the sublimable constituent in solid form. This is to be preferred where the sublimable constituent is desired as the final product. Where, however, the purpose is primarily to remove the sublimable constituent from the vaporous mixture in which it may occur as an undesirable impurity, substantially all of the advantages of the technique hereinbefore described can be realized by adding to the vaporous mixture any finely divided solid material which is inert to the mixture. Thus finely divided clay or quartz or various synthetic gels may be utilized, to improve heat transfer and to provide nuclei for the deposition of the sublimated material in accordance with the procedure herein described. Moreover, this technique can be utilized in the condensation of normally liquid materials from vaporous mixtures.

The nature and objects of the present invention having been thus described and illustrated, what is claimed as new and useful and is desired to be secured by Letters Patent is:

1. A method for recovering from a vaporous stream a contained product which is normally solid and capable of subliming which comprises passing the vaporous stream through a cooling zone maintained at a temperature suitable to effect solidification of the product in the presence of added
solid particles of the product, separating the solid product from residual vapors and feeding back some of said solid product to the vapor stream entering the cooling zone, while maintaining a sufficient velocity in said vapor stream to carry said recirculated solid along with such stream in a state of turbulent motion.

2. A method for recovering from a vapor stream a contained product which is normally solid and capable of subliming which comprises passing the vapor stream through a cooling zone maintained at a temperature suitable to effect solidification of the product onto added particles of the solidified product, removing the residual vapor stream and solidified product from the cooling zone, separating the solidified product from the vapor stream and returning a portion of said solidified product to the cooling zone together with a fresh quantity of vapor stream.

3. A method for recovering from a vapor stream a contained product which is normally solid and capable of subliming which comprises passing the vapor stream through a cooling zone maintained at a temperature suitable to effect solidification of the product onto added solid particles, simultaneously introducing into said cooling zone a finely divided solid, adjusting the rate of flow of said vapors and the rate of introduction of said solid so as to maintain in said cooling zone a density of said solid at least about 5# per cubic foot of vapor space, continuously removing vapor stream carrying entrained solid from said cooling zone and separating said solid from said vapor stream.

4. A method according to claim 3 in which the solid introduced into the cooling zone is the desired solid product capable of subliming.

5. A method for recovering from a vapor stream a contained product which is normally solid and capable of subliming which comprises passing the vapor stream through a cooling zone maintained at a temperature suitable to effect solidification of the product onto added solid particles, simultaneously introducing into said cooling zone a finely divided solid, adjusting the velocity of said vapor stream to said cooling zone to a value between about .5 and 5 feet per second and simultaneously adjusting the rate of feed of finely divided solid of at least 10# per cubic foot of vapor space, removing vapor stream carrying entrained solid from said cooling zone, and separating the solid from the vapor stream.

6. A method according to claim 5 in which the finely divided solid added to the cooling zone is the desired product capable of subliming.

7. A method for recovering from a vapor stream a contained product which is normally solid and capable of subliming which comprises passing said vapor stream through a line and thence into a cooling zone, establishing in a vertical column, in direct communication with said line, a head of fluidized finely divided solid whereby said fluidized solid is continuously fed into said vapor line and thence into the cooling zone wherein the sublimable material is solidified on said fluidized solid, recovering from said cooling zone a vapor stream containing said solid and separating said solid from said stream.

8. A method according to claim 7 in which the solid in the head of fluidized solid is the desired sublimable product.

9. A method for recovering solidified phthalic anhydride from a vapor stream formed by catalytic oxidation of an aromatic hydrocarbon, which comprises passing said vapor stream through a cooling zone, adding cooler preformed phthalic anhydride particles to said vapor stream being passed into said cooling zone, cooling the vapor stream containing phthalic anhydride vapor by heat transfer to the added solid particles and to cooling surfaces in said cooling zone without diluting the vapor by extraneous gas, solidifying phthalic anhydride from its vapor in said stream on to said added solid particles, concentrating and separating the resulting solid particle product into a dense fluidized phase from the remaining vapor stream leaving the cooling zone, and withdrawing a product stream of the resulting solid particles from said dense phase.

10. In the method of claim 9, the step of withdrawing a portion of the resulting solid particle product, further cooling this portion of the solid particle product, and supplying the thus cooled portion of the solid particle product as the preformed phthalic anhydride particles added to the vapor stream.

JOHN A. PATTERSON.

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