Oct. 1, 1957 C. L. DICKINSON 2,808,236

CRYSTALLIZING APPARATUS

Filed April 29, 1953

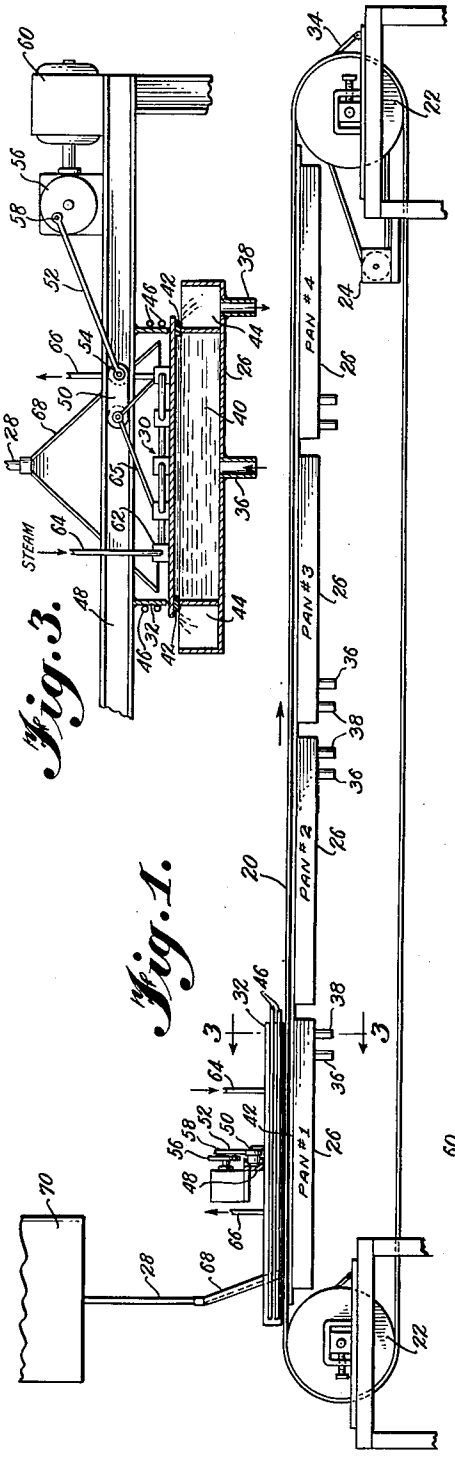

Fig. 1.

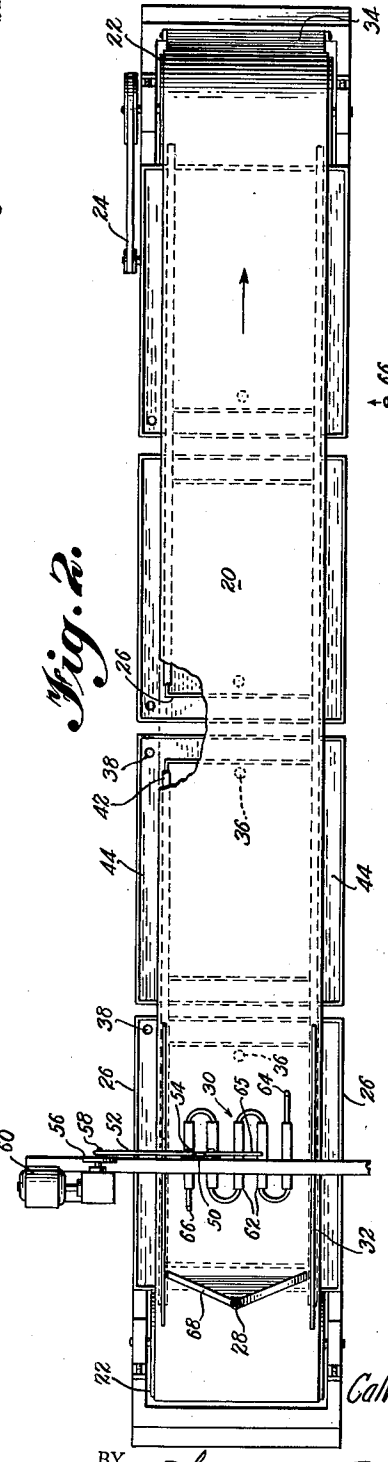

Fig. 2.

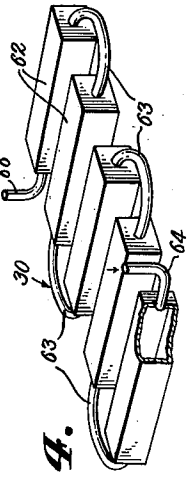

Fig. 4.

Fig. 3.

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CRYSTALLIZING APPARATUS

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11 Claims. (Cl. 257—6)

This invention relates to a new method and apparatus for the production of dichlorodiphenyl-trichloroethane in crystalline form.

As is well known, this material is widely used as an insecticide, the so-called para-para isomer (2,2 bis p-chlorophenyl 1,1,1-trichloroethane) having especially desirable properties in this respect. The material is produced commercially as a mixture of several isomers and the most commonly employed form is known as "technical DDT." This is a solid product at ordinary temperatures but melts readily below 100° C., usually at about 90° C. For convenience, dichlorodiphenyl-trichloroethane will be referred to hereinafter as DDT.

The invention is concerned particularly with the treatment of DDT to produce a crystalline product of such friable character that it may be broken up into particle form with a minimum of difficulty.

The patents of other inventors indicate the difficulty of crystallizing DDT in a form which may be readily ground or otherwise broken up. Thus, it is known that unless special crystallization technique is followed, a gummy, wax-like product results which cannot be ground to a form that flows freely, the ground product being a mass of sticky lumps. Such a product must be recrystallized until satisfactory or used in a liquid composition.

Other investigators have given the problem much attention as the solution to it is a matter of considerable commercial importance. Notwithstanding this, in practicing the known teachings of the art, it has not been found possible by me to achieve consistently a satisfactory commercial result without extensive modifications to the directions that are there given. It appears that some of the teachings are based upon pilot plant or laboratory scale operations and when it is attempted to adapt these teachings to commercial equipment, the product that is needed is not produced. The reason for this may be that it is either impossible in the practical sense to duplicate laboratory conditions in plant operations, or, it may be that there is not a teaching sufficient to accomplish a commercial operation satisfactorily. Whatever the reason may be, it is considered that the problem until this time remains unsolved. Aside from the unsatisfactory nature of these teachings in a technical sense, equipment that is suggested for carrying out the various methods involve an undesirably large capital investment, some requiring a series of drums that are expensive and not especially adaptable to the variety of conditions under which the general process is usually operated.

In contrast to this, the present invention teaches a method and apparatus which may be employed commercially with good success. A satisfactory commercial operation contains several requisites included in which are the production of a saleable product, an equipment investment which can be capitalized without economic embarrassment and an operating method and apparatus which will produce the material sufficiently rapidly in quantity with a minimum of attention from those who

have the responsibility of operating the plant. By this invention, such an operation may be achieved.

A short summary of the invention will be found helpful to further consideration.

In general the present invention contemplates depositing fused DDT as a layer upon a flat travelling surface, the DDT being at a temperature above its freezing point, and thereafter carrying it through a series of temperature reduction stages to a final crystalline state. In the interim between material deposition and material removal, proper rate of temperature reduction is specified which is accompanied by agitation in a manner and at a point which has been found to be of great importance to the accomplishment of the product that is desired. Crystallization of the mass will take place without agitation, but the product is not uniform, that is to say, portions of the mass will meet the desired specifications whereas other portions are gummy and unusable. Even if the unusable portions could be expeditiously separated from the other, the process without agitation would still remain undesirable economically. Stirring of a liquid to effect crystallization is, of course, not a new concept. On the other hand, simple stirring or agitation of a material that is moving at all times away from the agitating operation is not likely to result in a good product unless the agitating operation is carried out properly. Therefore, it is to the aspect of agitation, both in respect to the manner in which agitation cooperates in the over-all method that is employed and as to the apparatus which is hereinafter described that has been found satisfactory to effect the agitating action that this invention is to a large extent directed. Once the mass has reached the proper crystalline state, it is removed from the travelling belt in the form of large flakes as described at a later point herein.

In general, the apparatus comprises a travelling belt, the undersurface of which is maintained at a temperature considerably below the temperature of the DDT thereon. Cooling is accomplished by heat exchange with any suitable medium applied to the undersurface of the belt. Means is provided for distributing fused DDT in a layer on the belt as it flows from a storage point. An agitator is positioned above the belt and effects vigorous movement of the mass as it is carried across the agitator in the course of the operation. The agitator is located so as to perform its function in relation to a predetermined temperature drop, this being in the early stages of the supercooling of the mass. Means are provided for controlling the quantity and temperature of the cooling medium at several points along the length of the belt. Also, means are provided for removing the solidified product at the end of its period of treatment, and finally, the belt is provided with a variable speed driving mechanism so that the equipment may be adapted to a variety of environments as may be presented due to changing atmospheric conditions.

In the drawings,

Figure 1 is a view of the apparatus in side elevation;

Figure 2 is a plan view of Figure 1;

Figure 3 is a sectional view through upper portion of the apparatus taken on the line 3—3 of Figure 1;

Figure 4 is an enlarged perspective view partially in section of agitating apparatus forming a part of the invention.

Referring to Figures 1 and 2 of the drawings, numeral **20** denotes a thin continuous sheet which may be, for example, of stainless steel. Numerals **22** denote a pair of rollers, one being driven, positioned oppositely, upon which the belt is mounted and propelled in a continuous circuit. At numeral **24** there is illustrated in schematic fashion suitable means for driving the equipment. Numerals **26** denote a series of water pans that may be

maintained in position by any suitable supporting structure. Details of supporting structure are omitted for reasons of simplicity. Numeral **28** designates a material feeder from which DDT is deposited on the belt **20**. Numeral **30** designates generally the entire agitating apparatus, which includes the agitator itself as well as a suitable driving mechanism. Numeral **32** denotes a pair of upstanding oppositely positioned side walls mounted in contact with the travelling belt, which are for the purpose of maintaining the liquid DDT within the bounds of the belt so long as it is in liquid state. Numeral **34** denotes a material removing knife or doctor-blade which is for the purpose of flaking the material from the belt at the completion of its conversion to the desired crystalline state. The belt is driven at a uniform rate in a horizontal plane.

In Figure 3 which is a sectional view through the upper portion of the apparatus immediately forward of the agitator, numeral **36** denotes an inlet for water or other heat exchange medium and numeral **38** denotes the outlet therefor. Numeral **40** denotes the body of water which, as can be seen, rises to a point in contact with the undersurface of the belt **20**. Numerals **42** denote bearing surfaces on which the belt rests and travels. As can be seen, water is forced in through the inlet **36** and overflows the pan along its length, at both sides thereof between the bearing surface and the belt, into the outer trough which is denoted by numeral **44**. Trough **44** is continuous around each pan and all of the water therein drains away through outlet **38**. The pressure between the bearing surfaces and the belt is not especially critical but is not sufficiently great to stop the water flow.

Numerals **32**, which as indicated previously, designate oppositely positioned retaining walls forming a channel, are shown in section in this figure. Each side wall is supplied with a steam trace line, denoted by numerals **46** which are for the purpose of maintaining the side walls sufficiently hot that crystallization of DDT on them is prevented, thereby maintaining the channel free from crystalline DDT which woud gradually build up as the equipment is operated and, in so doing, materially interfere with the distribution of the mass and proper cooling thereof.

Positioned immediately above and upon side walls **32** is a track member denoted by numeral **48**. This member may take any desired form so long as it will permit accomplishment of the object which will immediately appear. Its purpose is to provide a suitable surface from which the agitating apparatus may be supported and operated. Here track member **48** is shown as a section of an I-beam. Numeral **50** denotes a bar which is slidably mounted in the channel of the I-beam. Pivotally connected to slidable bar **50** is a pusher-arm denoted by numeral **52**, it being connected to the bar as at numeral **54**. The opposite end of pusher arm **54** is pivotally mounted to eccentric **56** as indicated at numeral **58**. Numeral **60** denotes a driving means which is connected through a gear box to the eccentric **56** and thereby drives the same. It will be obvious that as the eccentric revolves, slidable bar will travel to and fro in track **48**.

Numerals **62** denote a series of agitator elements, rested upon belt **20**, that are connected to slidable bar **50** by any suitable means as indicated by numeral **64**. All of the agitator elements are interconnected and from the foregoing described arrangement it will be understood that they move in unison as bar **50** moves.

Referring in greater detail to the various components of structure embodied in the agitator member, attention is now directed to Figure 4 of the drawings which is a perspective view of the agitator elements **62**, one of which is shown in section. Each element is formed with a hollow interior to which steam is fed at one end, and after passing through the length of that element, passes to the next succeeding element through the end opposite to the point of feed. As can be seen more clearly in this figure, each agitator element is connected to the one next adjacent by small tubing or piping as at **63**. Observation of the drawing will reveal that a means for steam flow through the agitator is thereby provided, the steam being introduced in the first agitator element through line **64** and leaving the agitator through line **66** after the last agitator element has been traversed. The steam is fed to the agitator so as to maintain all points thereof which contact the liquid DDT at a temperature higher than crystallization temperature; otherwise the agitator becomes so clogged with crystalline DDT that the channel is obstructed and continuous operation is impossible. In fact, crystal build-up is so rapid on a cool surface that the operation could not be carried on more than a few minutes, a dam substantially across the channel being formed in that time.

While the agitator must be maintained at a suitably high temperature to the end as indicated above, in no event should its temperature be allowed to be such as to effect a substantial heating of the DDT. If this is permitted, crystallization will be seriously impaired.

It will be understood that steam line **64** must have a certain amount of flexibility in order to accommodate the movement of the agitator. In practice, a flexible line of any suitable material may be attached at a point adjacent the agitator for this purpose. The steam outlet line does not necessarily have to be flexible although it may be if desired. The line leads to a suitable open water collector. Steam pressure to the agitator is controlled by a simple valve arrangement not illustrated. Similarly, the flow of steam to trace lines **46** is valve controlled so that excessive cooling or excessive heating of the side walls does not take place.

Numeral **68** denotes a material distributor which leads to a point immediately above the travelling belt and provides a reasonably even distribution of the desired quantity of material upon the belt. Feed line **28** which leads from the storage tank **70** to the distributor **68** is insulated and heated so as to prevent crystallization in the feed line.

Doctor-blade **34** is of the conventional type employed in many flaking operations and the detail of it forms no part of this invention.

General construction of the belt system is well known to the art and it is not believed necessary to point out numerous details necessary for its satisfactory operation. However, it might be remarked that suitable adjusting means for the rollers **22** are usually provided so that proper tracking of the belt may be maintained. Furthermore, by the provision of suitable alarm mechanism that gives warning of improper belt tracking, the equipment may operate substantially unattended in this respect over long periods of time.

Agitator elements **62** may be of varying length; however, in the embodiment here contemplated, they are from 12 to 14 inches long and are spaced across the belt by a distance from each other of 3 to 4 inches. Agitator element length is a factor in effective agitation, and if the treated material is travelling rapidly, greater length may be desirable to provide a longer period of time in which a given unit of material is exposed to agitation. It has been found that when a belt of about 130 to 150 feet in total length is travelling at a speed of about three revolutions per hour with an agitator movement of about 60 to 70 cycles per minute, substantially all portions of the mass are given sufficient agitation to bring about uniform crystallization of excellent character, other requisites, hereinafter described, being observed.

While a single agitator has been suggested in the foregoing paragraphs, it is to be understood that a series of agitators may be employed. Additional agitators may be necessary especially if the travel speed of the belt is increased. As was indicated above, if the number of revolutions per hour of the belt is increased the residence time

of a unit part of the travelling DDT mass in the span of the agitator is decreased and its probability of receiving the necessary agitating action is thereby reduced. Consequently, additional agitators may be required. Agitator speed could be increased to accomplish the same purpose but as in any case the agitator produces quite a sloshing action, it may be found that the mass is too greatly disturbed by agitator speed increase. Entirely aside from the belt speed factor, additional agitation may be required due to material purity, temperature, atmospheric conditions, degree of crystal seeding, etc.

The water lines leading to the cooling pans are provided with flow control means, such as a simple valve, and temperature indicators are positioned in the lines.

It is contemplated that a commercial installation may utilize a travelling belt providing an upper horizontal surface of about 60 to 65 feet long. This affords sufficient crystallization time when moving at a speed of about 3 revolutions per hour under most conditions that need to be observed. Width of the belt is not believed to be critical to any extent and this dimension therefore may be related solely to the quantity of material that is desired to be produced.

Reference is now made to the operation of the equipment and the method attendant thereto by which the material is produced.

It should be understood that the apparatus and method of this invention is especially adapted to operation under conditions normally encountered in a commercial establishment. Such establishments are generally large, open and airy and unless special rooms are provided, processes are exposed to cold drafts at times which may affect them deleteriously. Additionally, while conditions falling within certain limits are contemplated and preferred, the attainment of such conditions continuously while operating the equipment and method in full scale production, even in specially provided space, presents problems. For example, normal atmospheric temperature variations which imposes room conditions may be from about 15° C. to about 35° C.; however, there are periods when the temperature may vary considerably from a contemplated normal range, that is to say, the equipment with the material thereon may be exposed to temperatures well below 15° C. for a period of time. If this occurs, and operational factors of the method and apparatus are not varied promptly to accommodate such an abnormal condition, a large quantity of material may be delivered to the doctor-blade for removal which is not of the standard that is desired by the industry.

It is also a somewhat difficult matter to maintain the method and apparatus in adjustment to varying conditions residing in or inherent in the operation. For example, those responsible for operating the equipment and the method may, due to conditions, possibly beyond immediate correction, deliver DDT to the travelling belt at a temperature much higher than the ideal temperature; they may provide heat exchange medium at too high or too low a temperature; they may allow the agitator to become too highly heated. When one or more of these circumstances is allowed to take place, it is desirable to salvage the material so treated, i. e., compensate for the error, prior to the time it is delivered to the doctor-blade for removal and storage, if it is possible to do so.

The method and apparatus of this invention are each adapted, one to the other, to the end that conditions may be so controlled as the material passes through the treating steps to the point of discharge that only considerable variation from the contemplated conditions must necessarily result in the production of a quantity of unuseable material.

While the conditions under which crystallization may be effected cannot be considered as extremely critical there are extremes of temperature that should be observed, and operational speed and other factors of the apparatus and method should be controlled within limits if a completely saleable product is to be obtained. It is found that the carefulness with which the conditions and factors are observed in operation are more critical at certain points than at others. There follows now a summary of the method of the invention wherein indications are given of the various factors and conditions that are important to successful practicing of the invention. In this summary, it is contemplated that atmospheric temperatures of between about 15° and about 35° C. prevails and that the belt of the apparatus provides an upper working surface of about 60 feet and is moving at about 7½ feet per minute. Further, it is contemplated that the depth of the layer of DDT will be of the order of about ½ inch or less and that it will have a transition point of about 90° C.

DDT is stored in a heated and insulated container near the travelling surface on which it is to be treated. DDT of commerce normally has a crystallization or transition point of approximately 90° C., and, in order for it to flow from a point of storage its temperature must be above about 90° C. The temperature of the material in storage may suitably vary between about 90° C. and about 120° C., preferably, however, between about 95° and and 105° C. Temperatures higher than these are not necessary and apparently do nothing but create additional problems in cooling.

In practicing the invention, fused DDT above about 90° C. is delivered to the travelling belt at a point near where the belt initially moves over the first pan. The temperature of the water in the pan may suitably vary over a rather wide temperature range as dictated by numerous factors. It is desirable to cool the material quite quickly at this stage of the procedure. If, for example, an unusually thick layer of DDT is being deposited on the belt, for example, more than about one-half inch, it might be necessary to maintain the temperature of the belt somewhat lower than for a thin layer of material. This circumstance can be compensated for by decreasing the speed of the belt. However, this slows production undesirably. Furthermore, it is preferable to maintain belt speed constant and vary other conditions of operation for, as the process is a continuous one, and as a belt speed at one time may be suitable to a given layer of material, its thickness, temperature, purity and other factors being considered, that belt speed might not be suitable for the conditions of the material deposited on the belt a short while later.

Ordinarily, water in the first pan may suitably be maintained between about 25° and 40° C., preferably, however, between about 30° and about 34° C.

The material on the belt moves across the first pan and is cooled to a temperature between about 50° and 70° C., preferably to a temperature of about 60° C. The temperature of the steam-traced sidewalls which form the channel is maintained suitably between about 90° and about 120° C., preferably between 95° C. and 105° C.

During the period of time in which the DDT is exposed to cooling in the first stage, it is subjected to vigorous agitation. As indicated previously herein the agitators are heated. Agitation of the mass may take place at any time after it has cooled below the normal transition temperature, between about 50° and about 90° C., more suitably between about 50° and about 70° C., and preferably at about 60° C. It is found that when agitation takes place at the lower temperature, more complete crystallization is achieved. No explanation for this is definitely known but it may be supposed that the effect of agitation is destroyed at a greater rate at higher temperatures than at lower temperatures. Additionally, as the agitator is heated to a temperature which may vary between about 85° C. and 120° C., preferably at a temperature of about 100° C., if the material is not cooled substantially below the transition point when it contacts the agitator the heat imparted thereto by the agitator

may be sufficient to prevent the desired cooling of the mass as it passes through the first stage, by which cooling it is made ready for actual setting and crystallization in the succeeding stages of the method. The relationship which should be maintained between the heat of the agitator and the coolness of the DDT should be such that the DDT is not heated to above 75° to 80° C. as it passes through the agitator, bearing in mind that the agitator should be maintained above the crystallization point of the material.

Generally, if the method and apparatus is operated within the limits above indicated and especially if they are operated under the specified preferable conditions, the mass will begin to crystallize a few seconds after agitation and about the time the travelling belt is transporting the material from above the first cooling pan. Conditions immediately following the first cooling stage are found to be quite important if a product of suitable character is to be obtained. It is found that great care must be exercised in regulating the rate of cooling that is permitted immediately after crystallization begins. It is found, for example, that sudden chilling of the mass or cooling too quickly brings about rapid crystallization of a substantial portion of the mass, but leaves the remainder in fused state which thereafter does not crystallize sufficiently, if at all, to prevent the product from being quite gummy and unusable for the purposes of this invention. Thus, if a body of cooling water is maintained in the second pan, any cooling effected thereby should be at quite a slow rate. Preferably, however, it is found that the second stage, herein termed the setting stage, should be allowed to take place under normal atmospheric conditions, that is to say, between about 15° and 35° C., suitably 20° to 25° C. for a period of time sufficient in length to bring about complete crystallization to the solid state. Generally about one to two minutes is sufficient for this purpose. Conceivably, as indicated previously, atmospheric conditions may be such that water, suitably warm to slow the cooling rate in the second stage, is necessary if heat interchange from the DDT at a sufficiently low rate is to be maintained. For this reason, and for the further reason that on occasion material is delivered to the second zone at a temperature higher than desirable, and thus may require cooling, the second pan is provided.

Ordinarily, by the time DDT has been transported through the setting zone, all problems relating to actually crystallizing the material no longer exist. However, quite often it is found in the operation of the apparatus and method that a thin layer of DDT adjacent the belt itself adheres quite strongly to the belt and there exists a problem of its removal. It is found that cooling of the belt after crystallization is substantially complete effects a release of the material from the belt without difficulty. Additionally, while it is difficult to establish the correctness of the belief, it is believed that the product is improved somewhat if it is continued to be cooled up to the point when it is discharged. This improvement, if any, seems to manifest itself in a product of greater hardness.

The degree of cooling, i. e., the total temperature drop, of the material, after it has left the agitator is not found to be especially critical to the production of a good product. As indicated previously, the temperature of the material in the agitator may be as high as 80° C. and the material may be flaked from the belt at a temperature as high as 55° C. and as low as desired. However, there is no reason for cooling the material below normal room temperature, i. e., about 20° C. to 25° C., so long as it is possible to flake the material from the belt. The following is a specific example of the method of the invention:

Example

DDT to a depth of about ⅜ inch is delivered to a thin stainless steel belt having an upper working surface approximately 60 feet long travelling at a rate of about 3 revolutions per hour. The temperature of the material as delivered is about 100° C. and has a transition point of about 90° C. The material is continuously discharged to the belt and as it passes across the first pan is exposed to indirect cooling by water maintained at a temperature of about 30° to 34° C. for a period of about 85 to 90 seconds. As the material is moved across the first pan and thereby cooled it is agitated by agitators oscillating laterally of the belt at a speed of about 70 cycles per minute the agitators being maintained at a temperature of about 100° C. The temperature of the DDT at the point of entry to the agitating members is about 60° C. The material is passed from the agitator and thence over the remainder of the first cooling pan. The steam-traced sidewalls which form the channel are maintained at about 95° C. The so-treated mass is delivered to the second setting stage of the method where it is allowed to cool still further under atmospheric conditions involving temperatures of about 20° C. for a period of time of about 85 to 90 seconds, during which time crystallization takes place effecting a solidification of substantially all of the DDT so treated. Thereafter, the material is passed over the third and fourth cooling pans which contain water at a temperature of about 60° C. The time of cooling and the passage of the material over the third and fourth pans is approximately 170 to 180 seconds, after which time the material is flaked from the travelling belt and delivered to a point of storage.

It is believed that those skilled in the art will be able to adapt the teaching as here given to the particular material to be crystallized and the variety of conditions under which the operation is carried out.

While there have been described various embodiments of the invention, the methods and apparatus described are not intended to be understood as limiting the scope of the invention as it is realized that changes there within are possible and it is further intended that each element recited in any of the following claims is to be understood as referring to all equivalent elements for accomplishing substantially the same results in substantially the same or equivalent manner, it being intended to cover the invention broadly in whatever form its principle may be utilized.

What is claimed is:

1. An apparatus for use in crystallizing DDT comprising a support, an endless, substantially flat, impermeable belt for receiving said DDT, said belt movably mounted on said support and adapted to travel continuously toward a DDT discharge zone, means for driving said belt, a heat exchanger adapted to cool said belt, an agitator positioned adjacent said belt so that liquid DDT on said belt can be agitated by motion of said agitator, said agitator comprising a series of elements spaced apart and adapted to be heated internally, said elements adapted to permit transport of DDT therebetween by said belt.

2. An agitator comprising in combination, a substantially flat, movable, impermeable endless belt and a series of elongated hollow elements arranged in substantially parallel, spaced apart relationship; means adapting said elements for heating and means for moving said elements as a group over said belt in a direction transverse with respect to the direction of movement of said belt.

3. An apparatus as in claim 1 wherein said agitator is adapted for movement transverse to the direction of belt movement and is located lengthwise of said travelling belt in relation to a predetermined temperature change in the DDT as effected by the said cooling means so that agitation of the said DDT may be had at an early stage in the cooling thereof.

4. An apparatus as in claim 1 wherein said cooling means comprises a series of pans arranged underneath said belt and adapted to accommodate water flow in contact with said belt.

5. An apparatus as in claim 4 wherein said agitator means comprises a series of elements spaced apart and

adapted to be heated internally and wherein means is provided for effecting motion of said elements transvesely with respect to the direction of said belt travel so that DDT thereon will receive agitation as it is carried between the said spaced apart elements by the said belt.

6. An apparatus as claimed in claim 1 including means for effecting motion of said elements laterally of said belt so that DDT thereon will receive agitation as it is carried between said spaced apart elements by the said belt.

7. An apparatus as claimed in claim 6 wherein said elements are hollow and adapted to be heated by steam passage therethrough, and wherein connecting means is provided for connecting the said elements together for movement in unison.

8. Apparatus as in claim 7 wherein said connecting means takes the form of pipe so that steam may be passed therethrough from one element to the next and thereby effect heating of the agitating means.

9. An apparatus as in claim 2 wherein said elements are hollow and adapted for internal heating.

10. An apparatus as in claim 9 wherein means is provided for carrying steam to the interior of each of said hollow elements.

11. An apparatus as in claim 10 where the last said means comprises pipe-sections, each section connecting two adjacent elements.

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