

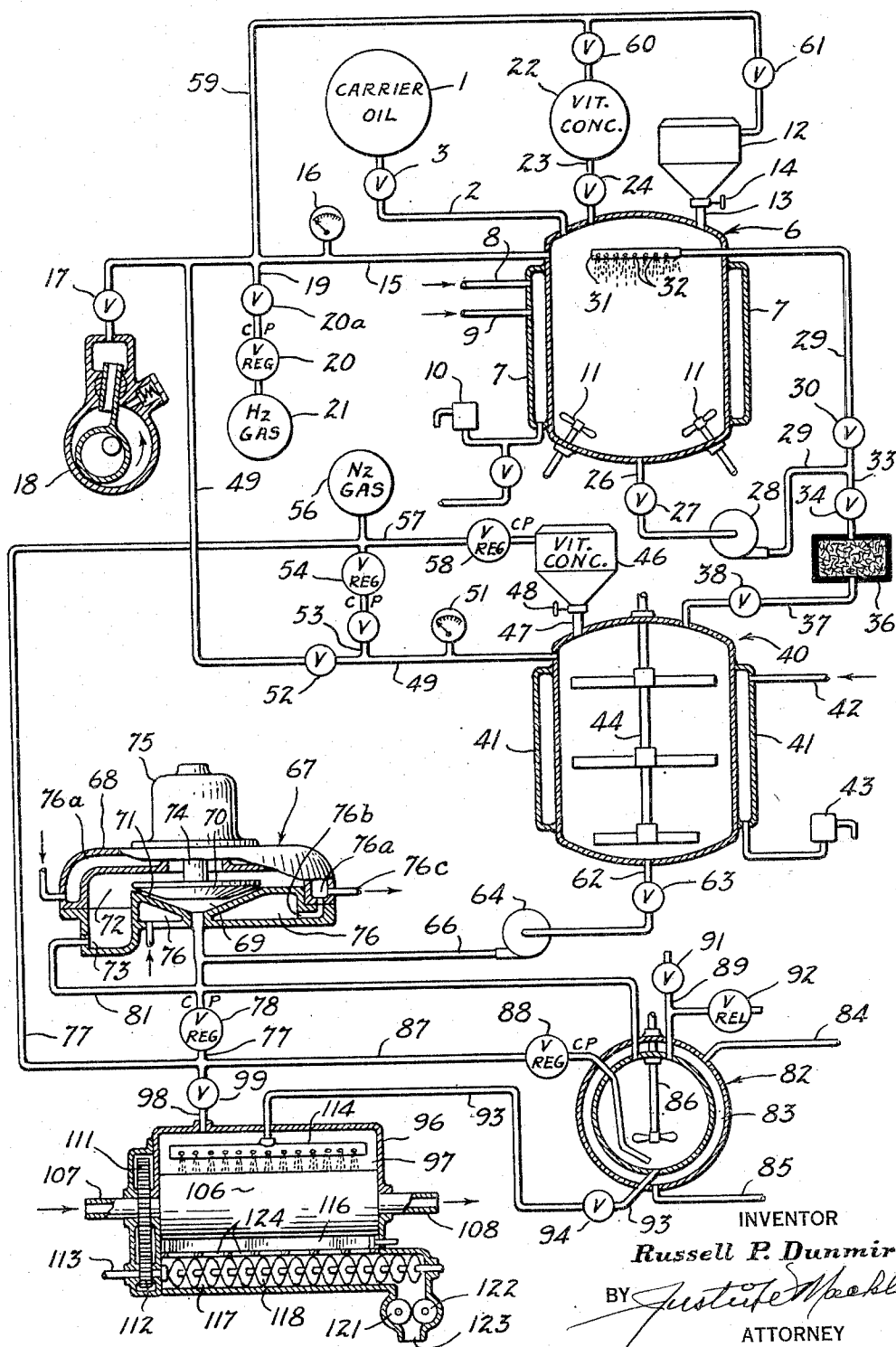
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R. P. DUNMIRE

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PROCESS FOR PRODUCING VITAMIN COMPOSITIONS

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PROCESS FOR PRODUCING VITAMIN COMPOSITIONS

Russell P. Dunmire, Orange Village, Ohio

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This invention relates to a system and apparatus for producing vitamin bearing compositions and particularly for producing such compositions having improved stability and uniformity.

It is well known that most vitamins deteriorate rapidly from the oxidizing effects of air, moisture, heat, and light and that the potency of vitamin compounds may be prolonged to a degree by incorporating them in a carrier oil that has been hydrogenated and then solidifying the mixture by cooling. However, attempts to prepare vitamin containing hydrogenated oil compositions of this character have been fraught with a number of difficulties, particularly when carrying out the processes in commercial scale operations.

When concentrates of oil-soluble vitamins in a fatty oil vehicle, such as fatty oil solutions of vitamins A, D, and E, are incorporated in a hydrogenated carrier oil and the mass is then solidified by cooling, the vitamins and their unsaturated vehicle tend to be thrown out of solution in the hydrogenated carrier oil and to sweat out to the surface of the solidified mass. This exposes them to destruction by oxidation and also to actual physical separation and loss during handling prior to actual consumption.

Various attempts have been made to prevent or minimize this result without notable success. For example, the oil-soluble vitamin concentrates have been adsorbed on and/or impregnated in various granular adsorbents or carrier solids. When charcoal is employed as the solid carrier, however, its adsorbing power is so tenacious that the digestive systems of animals and human beings are incapable of separating much of the adsorbed and absorbed vitamin content from the indigestible solid carrier.

When attempts have been made to employ other solid carriers of a mineral character having beneficial, or at least harmless, biological effects, such as calcium carbonate, difficulties have been encountered because of the presence of excessive quantities of impurities that have an oxidizing effect upon the vitamins or catalyze their oxidation. Even grades of such carrier materials of reagent quality are generally unsatisfactory in this respect. Many other mineral carriers are themselves incompatible with the vitamins because of their tendency to promote oxidation thereof.

Even when sufficiently pure calcium carbonate has been employed, however, the improvements in vitamin stability have been relatively slight due in part to incomplete impregnation of the mineral carrier with the vitamin concentrate. Hydrogenated fats normally crystallize as a single macro-crystal and the vitamins, or their unsaturated oil solutions, are thrown out of solution and collect on the surfaces of the crystal. If the granular materials, which are incompletely impregnated with the vitamins, are incorporated or mixed into a hydrogenated fatty oil carrier while still liquid, the carrier oil also penetrates the solid carrier material, dissolves a considerable portion of the vitamin content, and throws this

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vitamin material out of solution during solidification of the carrier oil, so that it still sweats out to the surfaces of particles of the final product, whatever their size may be. This action is facilitated by the need for granulating or otherwise comminuting the final product to render it susceptible to uniform mixing throughout masses of grains, mash, cereals and other similar feeds and foods. The comminution of the final vitamin product increases its surface area and facilitates the migration of the vitamins to the surfaces thereof.

A further difficulty is encountered in obtaining and maintaining a uniform dispersion of the granular carrier mineral during solidification of the carrier liquid. As a result, uniform composition of the final comminuted product has been difficult of attainment.

Attempts to minimize the difficulties in handling vitamin containing mineral granules by finer grinding have also met with little success. Unless closely controlled grinding, with size classification, is practiced at a prohibitive expense, uniformity of dispersion of the particles becomes difficult or impossible.

When water-soluble (oil-insoluble) vitamins, such as the B series and vitamins C and riboflavin, are mixed in granular form with a liquid, hydrogenated carrier oil, which is then solidified by cooling, difficulty is again encountered from settling of the solid vitamin materials before solidification is complete. When the solidified, vitamin bearing, carrier oil is ground, flaked, or otherwise subdivided into suitable form for admixture with foods to be fortified, the vitamin content of the particles of the final product is not uniform, and use of a given quantity of the product does not insure that the expected vitamin dose will be obtained.

Also, when the final solidified mass is subdivided, a relatively large proportion of vitamin granules, or vitamin containing granules, mixed through the mass become exposed at the surfaces of the particles of the finely divided product and are afforded little or no protection by the solidified carrier oil in which they were originally dispersed. Thus, a considerable loss of vitamin potency still results from oxidation of the vitamins exposed to light, air, moisture, etc., in this manner.

The term "vitamins," as used throughout this specification and in the claims, is intended to include the naturally occurring and synthesized true vitamin compounds and the so-called "pro-vitamins" which are capable of being converted by animals and human beings into the corresponding true vitamins during the processes of digestion and assimilation. Pro-vitamins are found in practically all vegetable matter, along with true vitamins in some cases. The sources of both the true vitamins and pro-vitamins are too numerous to mention and are well known in the art. Most commercial vitamin D and much of the commercial vitamin E, as well as some other commercial vitamins, are now synthesized. While the natural and synthetic vitamins of principal interest are the oil-soluble vitamins A, D, E, and carotene (pro-vitamin A) and the water-soluble B series, C, and riboflavin, other known vitamins of less common interest may also be advantageously processed in accordance with the invention and are intended to be embraced by the broad term "vitamins" as used herein.

The term "vitamin bearing oils," as used herein, is intended to include the fatty oils which contain, in solution, a substantial concentration of one or more vitamins which are naturally present therein. Examples of oils containing substantial amounts of vitamins naturally present therein are the various fish liver oils, wheat germ oil, palm oil, etc. These oils and the many other fatty oils from either animal or vegetable sources may have their content of soluble vitamins, such as vitamins A, D, and E, increased to any desired degree in ways well known

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in the art to produce vitamin enriched concentrates in which the liquid fatty oil merely serves as a protective vehicle and diluent.

The distinctions between the various types of oils involve differences largely of degree, as far as the content of oil-soluble vitamins is concerned. For convenience, the term "vitamin bearing oil" will be used herein only to designate oils having a natural vitamin content sufficiently great to be commercially useful in producing vitamin concentrates. Concentrates from these oils and oils to which large concentrations of oil-soluble vitamins have been added will hereinafter be referred to as "oil-soluble vitamin concentrates."

The term "carrier oils," as used herein, is intended to include the unsaturated fatty oils that are normally liquid, but are capable of being hydrogenated to a solid form, regardless of whether or not the oils contain naturally occurring vitamins. Examples of such oils containing only relatively small amounts of naturally occurring vitamins are soya bean oil, cotton seed oil, corn oil, animal fats, and fish oils generally. Examples of suitable carrier oils containing larger amounts of naturally occurring vitamins are the various "vitamin bearing oils" mentioned above.

The principal object of the present invention is to provide a system and apparatus for producing solidifiable, hydrogenated, carrier oils containing either or both oil-soluble and water-soluble vitamins uniformly dispersed throughout in a highly stable condition, which vitamin fortified oils may then be handled in any desired manner under an inert atmosphere to produce small size, solidified particles of selected or random sizes and shapes suitable for admixture with various foods and feeds.

More specific objects of the invention are to provide a system and apparatus for the foregoing purpose which avoids or eliminates the above described difficulties and problems of the prior art and which is efficient and reliable for commercial production of the vitamin containing compositions.

Still other objects and advantages of the invention will become apparent from the following specification and the accompanying drawing showing, somewhat schematically, the system and apparatus of the invention.

When employing the system and apparatus herein disclosed, the carrier oil should first be purified, as by heating and agitating the oil under vacuum, to remove as completely as possible all water, other volatile constituents, and dissolved gases that would deleteriously affect the vitamins to be incorporated therein by tending to promote their oxidation. It is also desirable that certain higher boiling constituents of animal and vegetable oils, such as resins, polymers etc., and all solid impurities of colloidal size and larger be removed by treating the oil with a suitable adsorbent, such as Fuller's earth, activated carbon, silica gel, or the like, followed by filtration.

The carrier oil may be a vitamin bearing, unsaturated, fatty oil, for example, wheat germ oil, palm oil, or cod or other fish liver oil; or the carrier oil may be an unsaturated fatty oil relatively low in vitamin content, such as soya bean oil, cotton seed oil, corn oil, fish oil, beef tallow, or the like. If a vitamin bearing oil is used as a carrier oil, the temperatures employed during the vacuum treatment should be kept as low as possible, preferably under 180° F., to avoid destruction of the natural vitamin content, and treatment with an adsorbent is generally to be avoided. When a non-vitamin bearing oil is employed, however, higher temperatures are permissible prior to the addition of vitamins thereto, and the purification may advantageously be carried out between about 250° and 350° F.

The vitamins to be added to the hydrogenated carrier oils in concentrated form may be either or both oil-soluble and water-soluble vitamins. In the case of oil-soluble vitamins, they are preferably added in the form of oil-soluble vitamin concentrates of the general character

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defined above; or powdered mineral carriers, such as calcium carbonate, may be impregnated with an oil-soluble vitamin concentrate and mixed with the oil.

The water-soluble vitamins may be incorporated in the carrier oil as finely divided solid powders; or water-solutions of the vitamins may be absorbed in a powdered mineral carrier, the mineral carrier and contained vitamins being then treated to remove all traces of water and any gases which would promote oxidation. After preparation, such powdered materials should be stored in vacuo or under a dry, inert gas until ready for use.

The use of powdered mineral carriers for the oil-soluble or water-soluble vitamins to be incorporated in the hydrogenated carrier and the treatment of the resulting mixture in accordance with the present invention combine to greatly enhance the protection against light and air afforded by the hydrogenated carrier oil.

Referring now to the drawing, there is shown, in diagrammatic form, the essential pieces of apparatus comprising my new system and the flow of materials through the various connecting conduits. Except as specifically mentioned hereinafter, the form of the individual pieces of apparatus may be conventional, and a detailed description of most of the individual pieces of equipment is unnecessary. The novelty of the present invention resides principally in new combinations of apparatus, the new combinations being capable of producing the improved results herein described.

My new system, in its simplest form, may comprise a tank 1 for an unsaturated fatty oil to be employed as a carrier oil. Any desired type of container for a suitably purified oil may, of course, be substituted for the tank 1, or it may be replaced by any suitable oil purifying system capable of supplying the purified oil as needed. A plurality of tanks or other sources of purified oil may be employed if desired and connected in parallel for supplying any selected one of several oils, or a mixture thereof, to the system.

As shown, the tank 1 is connected, through a supply conduit 2 having a suitable flow control valve 3 therein, to an autoclave 6 in which oil from the tank 1 is hydrogenated.

The autoclave 6 is equipped with both heating and cooling equipment, such as a steam jacket 7 to which a steam line 8, a cooling water line 9, and a suitable steam trap 10 are connected, for purposes hereinafter described. The autoclave is also provided with any suitable agitating means for maintaining the liquid contents of the autoclave in a constant state of agitation. The agitating means may include any desired number and arrangement of individual, propeller type, stirring devices 11 connected to suitable sources of power, or any other convenient type of agitator may be employed. An enclosed, gas tight hopper 12 is connected to the top of the autoclave 6 by means of a conduit 13 having a suitable valve or gate 14 for introducing finely divided solid catalytic material into the autoclave. A preferred form of catalyst for use in carrying out the present invention is a finely divided, activated, nickelous or platinum catalyst.

A conduit 15 equipped with a pressure gauge 16 leads into the autoclave 6 adjacent the top thereof and is connected through a valve 17 to a vacuum pump 18 for evacuating the autoclave. The conduit 15 also communicates through a branch conduit 19, having an adjustable pressure regulating valve 20 therein, with a source 21 of hydrogen gas under pressure whereby, when the vacuum valve 17 is closed, hydrogen gas may be supplied to the autoclave 6 at a pressure regulated by the setting of the valve 20.

A tank 22 for an oil-soluble vitamin concentrate may also be connected to the autoclave 6 through a conduit 23 and valve 24. This is optional depending upon the type of operation to be carried out, as will be explained hereinafter.

In order to circulate the liquid contents of the auto-

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clave 6 from the bottom to the top thereof, a conduit 26 having a valve 27 therein is connected at one end to the bottom of the autoclave and at its opposite end to the intake of a suitable pump 28. The outlet or high pressure side of the pump 28 is connected to a conduit 29, having a valve 30 therein, that leads upwardly and back into the autoclave 6 adjacent the top thereof where it is connected to a sprayhead 31. The sprayhead 31 is provided with a multiplicity of small openings 32 or any suitable non-clogging nozzle for discharging oil and entrained catalyst as a fine spray.

The liquid contents of the autoclave 6 may be withdrawn through the conduit 26 and pump 28 into a branch conduit 33, having a valve 34 therein, connected at one end to the high pressure side of the pump. The opposite end of the conduit 33 leads into a suitable filter 36 for removing entrained catalyst from the oil. The filtrate from the filter 36 is conveyed through a conduit 37, having a valve 38 therein, into a second autoclave 40 that may be generally similar to the autoclave 6. The autoclave 40 is equipped with any suitable heating equipment, such as a steam jacket 41 connected to a steam line 42 and a suitable steam trap 43. The autoclave 40 is also provided with a suitable agitator 44 for thoroughly mixing the contents thereof, a paddle or turbine type of mixer being indicated in the drawing in this instance. The agitator 44 may be mounted on a vertical shaft that extends through a suitable packing gland (not shown) in the top of the autoclave to any convenient source of power.

To permit the introduction of concentrated food supplement materials into the second autoclave 40, suitable sources of supply of these materials are connected by suitably valved conduits with the top of the autoclave. In this instance, only one such source 46 is shown with a conduit 47 and valve 48 associated therewith for introducing a desired quantity of food supplement material into the autoclave. The source 46 of food supplement material is intended to represent any desired number of enclosed hoppers or liquid receptacles for different food supplement materials which may be separately introduced into the autoclave through a plurality of separate conduits or which may be premixed and introduced together through the single conduit 47 shown in the drawing. Obviously many different arrangements for selectively introducing liquid or solid food supplement materials or mixtures thereof may be employed as equivalents of the single hopper or tank 46 and supply conduit 47. A conduit 49 having a pressure gauge 51 associated therewith is connected to the second autoclave 40 adjacent the top thereof for use in evacuating the autoclave and for supplying a selected gas thereto under pressure. For this purpose, the conduit 49 may lead to and join with the vacuum conduit 15 between the vacuum pump 18 and first autoclave 6. A valve 52 is provided in the vacuum conduit 49. Another conduit 53, provided with a pressure regulating valve 54, leads from a source 56 of an inert gas under pressure (nitrogen being preferred principally because of its low cost) to the conduit 49 for supplying gas to the second autoclave 40.

To facilitate the introduction of materials into the autoclave 40 while a positive gas pressure is maintained therein, a branch conduit 57 from the source 56 of nitrogen gas is connected through a valve 58 to the top of the hopper 46. Thus, the pressure in the hopper 46 may be maintained at least equal to that in the autoclave 40 to permit free flow from the hopper to the autoclave. For the same purpose a branch conduit 59 from the hydrogen tank 21 may be connected through valves 60 and 61, respectively, to the vitamin concentrate tank 22 and catalyst hopper 12.

For withdrawing the contents of the second autoclave 40, a conduit 62, provided with a valve 63, is connected at one end to the bottom of the autoclave and at its opposite end to the intake of a suitable pump 64. The

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outlet or high pressure side of the pump 64 is connected through a conduit 66 to a mill 67, which is preferably a colloid mill capable of subjecting a slurry of relatively fine solid particles in a carrier liquid to both shear and grinding forces and having suitable vapor seals for maintaining an inert atmosphere therein. As described below, the mill 67 may be required to reduce to colloidal size various solid food supplement materials supplied to the mill as a slurry or suspension. The mill may also be called upon to bring about the intimate mixing of a plurality of liquids, such as a mixture of a hydrogenated carrier oil and an unsaturated fatty oil containing dissolved food supplement materials. The purpose of the intimate mixing, as will be explained more fully herein after, is to bring about a sufficiently permanent dispersion of the oils and solids, if any, to prevent separation while they are still in a liquid state and to minimize any tendency toward separation after solidification of the mass.

Any of a considerable number of colloid mills of different design are suitable for the above described purposes with but minor modification. Since these mills are well known conventional types of machines, detailed descriptions of their various forms are unnecessary. In general, they are characterized by a mode of operation that involves feeding thin films of the liquid or slurry to be treated between closely spaced surfaces moving in opposite directions relative to each other at a high rate of speed.

The thickness of these films is controlled by the space between the relatively moving surfaces and, for the purposes of this invention, should be adjustable to cover a range of .0005 to .0025 of an inch. A spacing of about .0005 of an inch is preferred when the liquid contains no suspended solid material. When suspended solid particles are present, a somewhat greater spacing is required and .001 to .0025 of an inch is most suitable. Reduction of the solids to particle sizes in the range from about 2 to about 50 microns (capable of passing through about a 300-up mesh sieve) is preferred, though a maximum size of about 100 microns (capable of passing through about a 150-up mesh sieve) will still yield good results.

The required modification of most conventional colloid mills merely involves hermetically sealing the rotor chamber so that a moderate pressure of an inert gas may be maintained therein and jacketing the chamber so that the temperature of the material treated therein may be controlled by circulation of a suitable heat transfer medium. The temperature of the material entering the colloid mill may be kept above its solidification temperature by supplying sufficient heat from the steam jacket 41 of the autoclave 40, and in such case, only a suitable coolant need be supplied to the jacket of the colloid mill.

For illustrative purposes, one suitable form of colloid mill is diagrammatically shown in the drawing and will be briefly described. A housing 68 is provided with a centrally disposed inlet opening that leads into a chamber 69 defined by the housing. From the chamber 69, the liquid passes upwardly and outwardly between a conical rotor 70 and a stationary conical surface 71 carried by the housing and spaced from the rotor by the small clearance required as noted above. The liquid discharged radially outwardly from between the relatively moving conical surfaces is collected in a second chamber 72, defined by the housing, from which it is exhausted radially through an outlet 73. The rotor is driven through the shaft 74 which carries the rotor and extends upwardly through a suitable gas and liquid seal to a motor 75 mounted on the top of the housing. The lower part of the housing 68 around the stationary conical surface 71 is provided with a water jacket 76 connected to a source of cold water (not shown) for cooling purposes, since the operation of the mill at high speed and small clearance generates considerable heat

at the surface 71 that must be rapidly dissipated to prevent decomposition of the vitamins. The housing is also preferably surrounded by an additional jacket 76a having a separate connection with the source of cooling water. The two jacket portions 76 and 76a may communicate with each other at 76b in the vicinity of a common outlet 76c. Automatic temperature controls for the cooling water are desirable to simplify maintaining uniform temperatures.

A highly important feature of the invention is the provision and maintenance of an inert atmosphere in the colloid mill to prevent any of the liquid or slurry passing therethrough from being oxidized while spread out as a thin film between the relatively moving milling surfaces. For this purpose, a gas conduit 77 leading from the nitrogen gas supply line 53 is connected through a valve 78 to the chamber 69 below the rotor 70. By flowing nitrogen gas through the mill for a time prior to its operation and by employing a suitable pressure of nitrogen in the chamber 69 during its operation, the presence of oxygen from the air can be avoided and the milling operation can be safely performed.

The outlet 73 of the mill 67 is connected by means of a conduit 81 to an enclosed storage tank or reservoir 82 that also serves as a means for further adjusting the temperature of the material discharged from the colloid mill. For the latter purpose, the tank 82 is preferably provided with a jacket 83 for a suitable heat exchange medium that may be supplied thereto through a conduit 84 and exhausted through a conduit 85. In place of a steam jacket 83, any suitable arrangement of coils may be employed inside the tank 82 and any convenient form of agitator 86 may be used to facilitate rapid heat transfer.

For the purpose of maintaining an inert atmosphere over the contents of the storage tank 82, the source 56 of nitrogen gas is also connected to the tank by means of a conduit 87 provided with a valve 88; and a gas bleed-off pipe 89 is provided to permit purging the tank of all air before vitamin bearing oils are admitted. The pipe 89 is preferably provided with a manually operated valve 91 which may be opened to permit free escape of air and a pressure relief valve 92 which can be set to relieve excessive pressure and maintain a desired nitrogen pressure during normal operation.

The tank 82 is employed only for temporary storage and is provided with an outlet conduit 93, having a valve 94 therein, which leads to any desired form of apparatus for cooling a hydrogenated oil to solidify it and for granulating the solidified oil to a desired particle size for incorporation in or admixture with various types of foods and feeds. As shown for illustrative purposes, this apparatus may comprise a housing 96 defining an enclosed chamber 97 to which the selected inert gas from the source 56 may be supplied through a conduit 98 controlled by a valve 99.

Within the chamber 97 is mounted a hollow drum 103 that rotates on hollow stub shafts 107 and 108 suitably journaled in the housing 96. A cooling medium may be passed into the drum through one of the hollow shafts 107 and out of the other hollow shaft 108 for maintaining the surface of the drum at a desired temperature below the solidification temperature of the hydrogenated and fortified carrier oil.

One of the hollow shafts 107 carries a gear 111 that meshes with a second gear 112 on a drive shaft 113 coupled to any suitable source of power for rotating the drum 106.

The outlet conduit 93 from the storage tank 82 extends into the chamber 97 and terminates in a perforated distributing member 114 from which a multiplicity of fine streams of liquid may be discharged downwardly onto the drum 106. A knife or scraper 116 is mounted in the chamber 97 below the drum 106 and in contact there-

with for removing solidified material from the surface of the drum.

The housing 96 also defines a generally cylindrical chamber 117 containing a screw conveyor 118 directly connected to the drive shaft 113 and adapted to feed material along the chamber 117 to a pair of toothed grinding rolls 121 and 122 mounted in a discharge spout 123 of the conveyor chamber 117. Solidified material removed from the cooling drum by the scraper 116 is permitted to fall through openings 124 between the chambers 97 and 117 and be carried by the screw conveyor 118 to the grinding rolls 121 and 122, where the material is granulated and discharged from the spout 123 for packaging.

The above described solidifying and granulating apparatus is merely representative of one of many types of apparatus that may be employed to produce granules of a selected size from a solidifiable hydrogenated oil. The particular form of apparatus employed for this purpose may be selected in accordance with the size and shape of granules desired for different end uses.

The operation of the above described system in accordance with preferred practice of the invention will now be explained in detail.

Starting with all of the valves in the system closed, the valve 17 in the conduit 15 is opened, and the vacuum pump 18 is operated to reduce the pressure in the first autoclave 6 to about 5 mm. of mercury absolute. While the desired vacuum is being obtained, steam may be supplied to the jacket 7 to preheat the autoclave. The valve 3 is then opened to permit the autoclave to be charged to about the level shown in the drawing with a purified carrier oil from the tank 1. The valve 3 is then closed, the valve 27 in the conduit 26 and the valve 30 in the conduit 29 are opened, and the pump 28 is started. Oil withdrawn from the bottom of the autoclave through the conduit 26 is forced by the pump through the conduit 29 and back into the top of the autoclave as a fine spray from the sprayhead 31.

During this operation, the vacuum pump is maintained in operation and in communication with the autoclave to maintain a vacuum of approximately the order indicated for withdrawing from the oil as much of its original content of dissolved gases and light volatile constituents as possible. At the same time, the supply of steam to the jacket 7 is regulated to bring the temperature of the oil up to the selected hydrogenation temperature and hold it there. Substantially complete degasification of the oil is promoted by the combined effects of the heat supplied, the vacuum, and the continuous circulation of oil for maintaining a fine spray of oil above the liquid level in the autoclave.

After degasification of the oil in the manner described, the valve 17 in the conduit 15 is closed, and the pressure regulating valve 20 in the hydrogen line 19 is opened to bleed hydrogen gas into the autoclave. The valve 20 is set to build up and maintain a hydrogen pressure in the autoclave of about 30 pounds per sq. inch gauge. With the circulation of oil continuing and the hydrogen pressure maintained, the oil becomes saturated with hydrogen gas at the temperature and pressure employed.

The agitators 11 are then started in operation, and a suitable amount of a catalyst from the supply source 12 is charged into the autoclave to initiate the hydrogenation reaction. By continuing the circulation of oil and suspended catalyst through the circulation system while maintaining the pressure of hydrogen in the autoclave, additional hydrogen gas is dissolved in the oil as needed, and substantially complete hydrogenation may be accomplished rapidly and efficiently.

If a concentrate of one or more oil-soluble vitamins in an unsaturated fatty oil vehicle is to be incorporated in the hydrogenated carrier oil, the concentrate is preferably introduced into the carrier oil in the first autoclave 6 in the presence of the catalyst and an ample supply of hydrogen gas in order also to hydrogenate the oil vehicle

of the concentrate. To do this safely, however, a much lower temperature is necessary than that used to hydrogenate the carrier oil. Accordingly, the temperature of the carrier oil in the autoclave 6 is reduced at least as low as 180° F. and preferably to about 150° F. by cutting off the supply of steam to the jacket 7 and substituting water or other suitable coolant through the conduit 9. Rapid cooling is facilitated by the agitation and circulation maintained by the agitators 11 and the pump 28. The valve 24 in the conduit 23 is then opened to supply a predetermined quantity of the oil-soluble vitamin concentrate to the autoclave 6 from the tank 22. Hydrogenation of the small quantity of concentrate oil vehicle is rapidly effected even at the lower temperature, and no appreciable circulation time need be provided after the vitamin concentrate has been added.

When the desired degree of hydrogenation has been accomplished, with or without the addition of an oil-soluble vitamin concentrate, the hydrogen regulator valve 20 may be closed and the vacuum valves 17 opened, while continuing the circulation of oil through the conduit 29, to remove unreacted hydrogen gas from the oil in the same manner that degasification of the oil was originally effected. The vacuum pump 18 may simultaneously be connected to the second autoclave 40 through the conduit 49 to reduce the pressure therein to about 5 mm. of mercury absolute. Then the vacuum pump is disconnected from both of the autoclaves by closing the valve 17, and the vacuum pump 18 is turned off. At this point, a selected inert gas, preferably nitrogen, is bled into both autoclaves by opening and setting the valve 54 to maintain a pressure of, say, 5 pounds per sq. inch gauge for saturating the hydrogenated oil in the first autoclave 6 with nitrogen and providing an inert atmosphere in the second autoclave 40. During this operation, the second autoclave 40 may be preheated to a temperature sufficient to maintain the hydrogenated oil in the liquid state.

By closing the valve 30 in the circulating system and opening the valves 34 and 38 in the conduits 33 and 37, respectively, the hydrogenated oil and suspended catalyst are pumped to the filter 36 for removal of the catalyst. The filtrate oil passes from the filter through the conduit 37 and into the second autoclave 40 where it is protected by the nitrogen atmosphere therein and is held at a temperature sufficient to maintain its liquid state. At this point, the valves 34, 38, and 52 may be closed to isolate the first autoclave 6 from the remainder of the system.

With the agitator 44 in operation, the valve 48 in the conduit 47 may be opened for introducing the desired vitamin concentrates into the autoclave 40 from the source or sources of supply 46. As explained above, any number of vitamin concentrates in any or all of the liquid or powdered forms described may be supplied in this manner in amounts sufficient to provide a predetermined final concentration of each of the vitamins in the final product. Mixing by means of the agitator 44 is continued until thorough dispersion of the added vitamin compositions in the hydrogenated carrier oil is effected.

During mixing of the materials in the autoclave 40, the nitrogen control valve 78 in the conduit 77 and the storage tank bleed-off valve 91 are opened to permit nitrogen to flow for a time through the colloid mill for driving as much air as possible out of this part of the system and out through the bleed-off valve 91. Then the valve 88 in the conduit 87 is also opened to more thoroughly drive air out of the storage tank 82. After this, the bleed-off valve 91 is closed and the pressure regulator valve 92 is set to permit a constant slow escape of nitrogen from the storage tank 82.

When thorough mixing of the vitamin compositions added to the autoclave 40 has been accomplished, the valve 63 in the conduit 62 is opened, and the mill 67 and pump 64 are placed in operation to convey the contents of the autoclave 40 through the mill for more complete and intimate dispersion. As noted above, if solid

materials are present in the hydrogentaed oil, the mill is adjusted to reduce the solid particles to a maximum size of about 100 microns at the selected rate of flow there-through. If no solid materials are present in the oil, a closer setting of the colloid mill is desirable for insuring substantially permanent blending or homogenization of the vitamin oil concentrates and the hydrogenated carrier oil. The degree of blending or homogenization should be sufficient to prevent separation of the constituent oils for as long as they may be held in a liquid state during storage. This degree of homogenization, therefore, is appropriately termed "substantially permanent marriage."

The output of the mill 67 is passed through the conduit 81 into the storage tank 82 where the vitamin enriched material is held in the liquid state by heat supplied from the steam jacket 83. As needed, or as determined by the capacity of the apparatus for solidifying and granulating the product, the contents of the storage tank 82 may be drawn off and fed through the outlet conduit 93 to the distributor 114 in the cooling chamber 97. The liquid product is discharged from the distributor 114 onto the cooling drum 106, in the presence of an inert atmosphere provided therein by cracking the valve 99 in the conduit 98 to bleed nitrogen constantly through the granulating apparatus. The liquid product is solidified on the drum 106 to a film thickness determined by the rate of feed from the tank 82 and the speed of rotation of the drum. This film is removed from the drum and disintegrated to a considerable extent by the scraper 116, and the material falls through the openings 124 and into the conveyor chamber 117. It is then conveyed by the screw conveyor 118 to the granulating rolls 121 and 122 and is finally discharged from the spout 123 as a stable vitamin concentrate effectively protected from deterioration by the solidified, air and moisture impervious carrier oil in which it is dispersed.

The system and apparatus described and illustrated herein has a number of characteristics that render it capable of producing more stable vitamin compositions than prior art systems. The foremost of these characteristics is the action of the colloid mill 67. The prior art of which I am aware has been unable to obtain substantially permanent marriage of hydrogenated carrier oils and added oil-soluble vitamin concentrates. Upon solidification of the vitamin carrier oils, the oil-soluble vitamin concentrates have separated and bled to the surface so persistently that only very temporary protection has been afforded by the carrier oil, particularly when the product is finely granulated. No amount of simple mixing, regardless of its violence or duration, has been of any material assistance, and even conventional homogenizers have produced only slight improvements in stability.

When a mixture of the still liquid carrier oil and the added oil-soluble vitamin concentrates is passed through a colloid mill of the general character described, however, the high molecular shear produced on a thin film of the mixture somehow produces a marriage of the components that survives indefinite storage in the liquid phase and subsequent solidification without any appreciable tendency toward separation or bleeding of the oil-soluble vitamins to the surface of the finest particles to which the final product may be reduced.

The explanation of this startling change in the normal behavior of such mixtures is not thoroughly understood. The character of the shearing action of the colloid mill on films of the order of .0005 to .0025 of an inch in thickness, however, produces what appears to be an entirely different kind of union of the components of the mixtures than has been obtainable with any other known type of mixer.

Since the operation of a colloid mill with the small clearance required generates considerable heat, it is important that this heat be dissipated rapidly and that the milling operation be performed in a carefully controlled inert atmosphere. Otherwise, though the desired marriage

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of the components of the mixture is obtained, the vitamins are likely to be oxidized or even decomposed. Accordingly, the importance of controlling the temperature within the colloid mill and maintaining an inert atmosphere therein cannot be overemphasized.

To illustrate the beneficial effects of the above described operations on the stability of the final product, compared to products similarly prepared but without employing a colloid mill or the like, reference is made to the following examples:

Example 1

Pro-vitamin A was incorporated in a hydrogenated oil using the apparatus and procedure described above, and a sample of the product was compared with a sample of the same ingredients prepared in the same manner under identical conditions except for elimination of the colloid mill from the system.

In both cases, the carrier oil was a fish oil having a melting point of 140° F., substantially completely hydrogenated at about 270° F. in about two hours and 40 minutes in the presence of a nickelous catalyst in the first autoclave. The hydrogenated carrier oil was filtered to remove the catalyst and passed into the second autoclave where, under a nitrogen atmosphere, a pro-vitamin A concentrate of 200,000 I. N. U. per gm. (crude carotene) was added in sufficient quantity to produce a final concentration of 5,000 I. N. U. per gm. of product. In one case, the vitamin fortified oil was passed through a Premier type of colloid mill having a 6 inch rotor turning at 3600 R. P. M. with a clearance of .0005 of an inch. A nitrogen atmosphere was maintained in the mill throughout the operation, and the output of the mill was sent to storage under a nitrogen atmosphere until withdrawn, cooled to the solid phase, and granulated to pass through a 100-mesh sieve. A sample of this material was taken and will be referred to as sample No. 1. In the other case, the vitamin fortified oil from the second autoclave, after thorough mixing therein under a nitrogen atmosphere, was sent directly to storage (by-passing the colloid mill) and handled the same as the material of sample No. 1. A sample taken from this latter batch that was not passed through the colloid mill will be referred to as sample No. 2.

Samples Nos. 1 and 2 were lightly washed with petroleum ether to dissolve all of the pro-vitamin A that had migrated to the surface of the fine granules. The granules were then tested for their pro-vitamin A content. Sample No. 1 was found to have lost less than 2% of its original pro-vitamin A content, whereas sample No. 2 lost about 80% of its pro-vitamin A content.

The vast difference in the ability of the two samples to retain the pro-vitamin A within the hydrogenated carrier fat was due solely to the effects of the colloid mill treatment of the material from which sample No. 1 was taken.

Example 2

Tests similar to those described in Example 1 were performed with a cotton seed carrier oil, substantially completely hydrogenated at about 270° F. in about 5 hours. In the second autoclave, a pro-vitamin A concentrate of 200,000 I. N. U. per gm. (crude carotene) was added in an amount sufficient to give a final concentration of 5,000 I. N. U. per gm. of product; a vitamin D₃ concentrate of 100,000 I. N. U. per gm. in a cotton seed oil vehicle was added in an amount sufficient to give a final concentration of 1,000 A. O. A. C. units per gm. of product; and a vitamin E (alpha tocopherol) concentrate of 340 mg. per gm. in a cotton seed oil vehicle was added in an amount sufficient to give a final concentration of 8.5 mgs. per gm. of product. The mixture was thoroughly stirred until apparently homogeneous. In one case, the mixture was then passed through the colloid mill, as in Example 1, in the course of producing sample No. 3, and in another case the colloid mill treatment was omitted in the course of producing sample No. 4.

Samples Nos. 3 and 4 were lightly washed with petro-

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leum ether and tested for their retained vitamin content. Sample No. 3 was found to have lost less than 2% of its original content of each of the vitamins A, D₃, and E, whereas sample No. 4 was found to have lost about 60% of each.

By adding the oil-soluble vitamin concentrate to the carrier oil in the first autoclave 6 in the presence of the catalyst, the unsaturated vehicle of the concentrate is also hydrogenated. This increases its miscibility with the carrier oil and produces still further stability of the final product. However, the further improvement obtained seems to be greater than can be explained by improved miscibility alone, for the product is far more resistant to adverse storage conditions, such as abnormally high temperatures and lack of adequate protection from light and air. The explanation of this further improvement may be that the vitamin compounds themselves, being unsaturated hydrocarbon compounds, are also hydrogenated, at least in part, and thereby rendered more stable. Whatever the full and correct explanation may be, however, this mode of adding the oil-soluble vitamin concentrate is most effective in improving the stability of the product. Provision of facilities for adding the oil-soluble vitamin concentrates in the presence of the hydrogenation catalyst, therefore, is still another important feature of my new system and apparatus.

As is readily apparent, the second autoclave may be bypassed or serve merely as a part of the conduit line leading to the colloid mill if no solid food supplement materials are to be incorporated in the hydrogenated oil after adding oil-soluble food supplement material in the first autoclave, as described above.

When powdered vitamin concentrates, such as any of the forms mentioned above, are added to the carrier oil in the second autoclave 40, with or without the addition of oil-soluble vitamin concentrates in liquid form, the mixer 44 in the second autoclave 40 is relied upon to disperse the solid particles temporarily in the carrier oil. The size of the solid particles is necessarily too large for them to be suspended for long periods of time in the carrier oil without settling because very fine grinding of the particles prior to incorporation of them in the carrier oil would not be feasible due to the destructive effects upon the vitamin compounds of the heat generated in the grinding operation.

When the temporary dispersion of the solid particles in the carrier oil is passed through the colloid mill 67, however, reduction of the particles to colloidal sizes ranging below 100 microns, and preferably below 50 microns, is readily accomplished without harmful effects. The output of the colloid mill consists of a dispersion in which the colloid size solid particles will remain uniformly in suspension for prolonged periods of time in the storage tank 82, and the uniform composition of this dispersion will be maintained during solidification in the cooling chamber 97 and during granulation of the solid product to the desired final particle size.

The ability of the colloid mill to produce a dispersion of solid particles that will resist settling or separation during storage and during solidification not only results in a product of uniform composition throughout, but also results in a product that is substantially improved as regards the stability of the vitamin compositions introduced in solid form into the second autoclave 40. Whether this improvement in stability is due entirely to the fineness of the dispersion of the colloidal size particles, or is due in part to additional phenomena inherent in the colloid mill operation, is difficult to determine. The intimate molecular contact between the carrier oil and the solid vitamin particles during the milling operation and the presence of the inert gas intimately dispersed in the mixture as it is being milled, appear to combine in their effects to provide a kind of inter-molecular association affording an entirely different type of protection of the vitamin compositions than would be expected from mere considerations of particle size of the solids.

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The advantages resulting from the colloid mill treatment, when water-soluble vitamin compounds in solid form have been introduced into the carrier oil, are indicated by the following example:

Example 3

A fish oil was hydrogenated in the first autoclave 6 in the same manner and to the same degree as in Example 1. After removal of the catalyst in the filter 36, the hydrogenated oil was introduced into the second autoclave 40, where 350 mg. of riboflavin was added in the form of a fine powder and was stirred by means of the mixer 44 until uniformly dispersed in the oil. Sample No. 5 was taken directly from the second autoclave 40, cooled under a nitrogen atmosphere to solidify the mix, and granulated under a nitrogen atmosphere to particle sizes passing through a 100-up mesh sieve. Sample No. 6 was taken directly from the second autoclave 40 and was passed through the same colloid mill set for a clearance of .0015 of an inch and run at 3600 R. P. M. while maintaining a nitrogen atmosphere therein. The output of the colloid mill was granulated in the same manner as sample No. 5 and to the same range of particle sizes.

When samples Nos. 5 and 6 were washed with water and then tested for their riboflavin content, sample No. 5 lost approximately 10% of its initial riboflavin content, whereas sample No. 6 showed no detectible loss of riboflavin.

From the foregoing it will be appreciated that I have provided a system and apparatus adapted for use in the production of solidified hydrogenated carrier oils containing any of a variety of forms of both oil-soluble and water-soluble vitamin concentrates. It will also be appreciated that the preparation of the product may be carried out in my new system and apparatus in such a manner as to produce a vastly improved product as regards both the stability of the vitamin compositions and the uniformity of their dispersion throughout the granules of the final product, thus overcoming or avoiding the aforementioned serious difficulties and defects of the prior art.

While this application is directed to the system and apparatus, as defined in the appended claims, various features of the process as performed in such a system and apparatus are disclosed and claimed in my copending application for Process of Producing a Stabilized Vitamin Compound, Serial No. 20,748, filed April 13, 1948, now abandoned.

The present application is a continuation-in-part of my prior application for Apparatus for Producing a Stabilized Vitamin Compound, Serial No. 522,515, filed February 15, 1944, now abandoned.

While various details of a preferred form of system and apparatus have been disclosed for illustrative purposes, it is obvious that many changes in such details may be made within the scope of the invention and that various sub-combinations included in the complete system may be separately employed to accomplish more limited objectives.

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Having described my invention, I claim:

1. A process for stabilizing the substantially anhydrous combination comprising a vitamin and a hydrogenated oil which comprises subjecting the combination in a liquid state prior to solidification to a colloidal grinding action while maintaining the liquid in an inert atmosphere whereby the liquid combination is subjected to high shearing forces while flowing in a thin film.
2. The process of claim 1 in which the vitamin is oil-soluble.
3. The process of claim 1 in which the anhydrous combination is substantially entirely liquid except that the vitamin is a finely divided solid.
4. The process of claim 1 in which the vitamin is riboflavin.
5. The process of claim 1 in which the hydrogenated oil is hydrogenated fish oil.
6. A process for producing and stabilizing a substantially anhydrous composition comprising a vitamin and a hydrogenated oil, which comprises heating the oil and removing air and impurities and products of previous oxidation from the oil by adsorption, then cooling the oil to approximately 150°, and then while maintaining it in a liquid state and in an inert atmosphere introducing the vitamin content, and subjecting the liquid composition to a colloidal grinding action of high shearing forces while still in an inert atmosphere, and thereafter causing the same to solidify in the absence of air.

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