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METHOD OF MAKING SUBSTANTIALLY ANHYDROUS FINELY-DIVIDED SYNTHETIC RESINS

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This invention relates to methods of making substantially dry and anhydrous synthetic resins of the potentially reactive type, useful in the arts as binders, plastic molding materials, lacquers and varnishes, when made from sticky, tacky, sludgelike resinous masses containing relatively large quantities of occluded water or mother liquor.

More specifically the removal of such volatile content is accomplished substantially without heating to a high temperature and therefore without polymerizing the resinous material further. This result is attained by reducing the sludgelike mass to very small particle sizes and keeping this finely divided mass in constant motion in the presence of air until sufficient volatile material is removed and the particles lose their tendency to cohere. Further drying may thereafter continue to reduce the volatile content to practical requirements. This makes it possible to produce resins of very low melting point, having a light color and being readily soluble in the usual organic solvents. Resins of high reactivity may be made without noticeable change in the product.

My preferred method consists in the steps of (1) removing heat from the sludgelike mass to a temperature low enough to produce a hard, grindable solid; (2) grinding the cooled mass into small particle sizes; (3) keeping the ground resin in motion while being subjected to the drying action of air currents until the resinous particles will no longer cohere; (4) continuing the drying to remove volatiles to a further degree if desired.

For the freezing of the resinous product most any method of quickly removing the heat from the resinous mass may be used as for example cold liquids, ices and mechanical refrigeration. Preferably it is most advantageous to use mechanical refrigeration in order to remove the heat from the mass rapidly and to cool well below the freezing point of the mass. The mass may be frozen in the digester or in drums or other containers such as pans, thin layers, etc.

By cooling the resinous mass in the digester to a consistency which will still enable the material to flow, the kettle product will consist of two layers, a lower resinous layer containing occluded water and uncombined reagents to the extent of about 20% of the dry resin weight and an upper or supernatant layer containing the mother liquor consisting chiefly of water. This upper layer may be removed if desired but if the resin is removed from the bottom of the digester the supernatant watery layer may be disposed of after the resinous layer has been removed or blown out.

As the resin flows from the kettle it is preferably formed into thin layers as by being pumped under a pressure of from 50 to 2000 pounds per square inch through an oblong orifice onto a cooling belt carrying the product through the refrigerator. When sufficiently cooled the product is delivered by the conveyor belt to the crusher and grinder.

A high pressure double screw type pump is preferably used for the pressure and extrusion operation referred to in the preceding paragraph. The pressure required will vary with the shape and size of the orifice used and the consistency of the resinous material.

An impact pulverizer having air separation means is well suited for the grinding of the product. The resin separated from most of the air has lost much of its volatile constituent. Should the ground particles be sticky the powder should be kept in motion to prevent lumping, etc. An atmospheric shelf, or else a trough dryer may be used for the final drying. The product may be reground and if necessary redried.

In the grinding and drying operations the air may be heated to facilitate the removal of moisture as the moisture is present mostly on the outside of the powdery particles and therefore surface evaporation really lowers the temperature of the resinous powder. Care must be taken not to heat the air to the point where the resin will melt and fuse as it is extremely difficult to remove occluded moisture from large bodies of the resin.

The subdivision of the wet, sludgelike, sticky resinous mass into fine particles and keeping the product in such fine subdivided condition until sufficiently altered to a non-tacky powdered mass forms the basis of the

method described herein. By this method resins of extreme reactivity may be made on a large production basis with extreme uniformity. The ease of handling of a two ton digester load of resin is so simple that no hazards are encountered and there are no losses of material because of the reaction becoming uncontrollable or because the occluded volatiles cannot be removed in time before the viscosity of the product is too high.

The method eliminates the difficulties encountered because of the mass action of a sticky product of relatively poor heat conductivity.

By my method I eliminate the difficulties encountered in the one step wet reaction and am enabled to use the same cheap wet starting materials of such process with an increase in the production and produce products which are more useful and uniform.

The two step method of resin manufacture was an improvement on the old wet one step system as the resin produced was permanently fusible and of low viscosity. The use of the subsequent hardening agent added to the resin mass is both expensive and undesirable. The hexamethylenetetramine used is expensive and cannot be added to the hot resin mass in the digester. If mixed with the ground fusible resin the mixture separates in time, causing endless troubles from lack of uniformity. To produce a fairly uniform composition the resin and hardening agent must be ground together for a number of hours in a ball mill, a dusty noncontinuous operation. The liberation of the large quantities of ammonia during reaction makes the use of hexamethylenetetramine impossible for certain purposes where the electrical requirements are high. The product is useless for lacquers either alone or in cellulose compounds as the resin is not tough and if reacted to combine with the hexamethylenetetramine bubbles are formed on the surface if cured at atmospheric pressure, the hexamethylenetetramine constantly reduces the viscosity of the nitrocellulose solutions. This is a desirable attribute when and if wanted as where high viscosity cellulose is used but it is difficult to stabilize and maintain the desired viscosity.

The one step dry reaction eliminates many of the difficulties of the preceding methods but it is expensive and it is difficult to produce a product of low viscosity and free from large amounts of ammonia liberated by the hexamethylenetetramine used. The reaction is essentially conducted in an ammonia system instead of water and therefore several of the objections to the wet one step method remain.

The resinous product made by my method impregnates paper and fillers well without the use of solvents or differential rolls. Therefore laminated sheet, tube and gear products can be made without the use of solvents.

As a lacquer or varnish ingredient the product adheres well to the support, has a hard surface and is very soluble in the solvents used. When heated there is produced a fine polished film free from bubbles and of uniform transparency.

While the method is directed chiefly to the production of resinous masses from phenols and formaldehyde, other phenolic bodies or homologues may be used such as the cresols, naphthols, resorcinol and xylenols. In place of formaldehyde other bodies having active methylene groups, other aldehydes and their derivatives and other resin producing bodies such as the carbohydrates, starches, sugars and higher alcohols such as glycerine may be used in the production of useful resins by my method.

The "glyptal" resins made by combining polyhydric alcohols such as glycerine with suitable polybasic acids such as phthalic anhydrid, etc., likewise, the various urea resins as for example those made from urea and formaldehyde may be advantageously processed by my method to produce resins and plastic moldable masses free from bubbles and other faults.

As the many formulæ now published and known can be used in my process it is not necessary to give detailed examples of these as the method clearly specifies the handling of the resinous masses made by any well known method. The addition of various solvents, colors, dyes, plasticizers, modifiers, accelerators, hardening agents, fillers or extending materials may be made before, during or after the reaction and treatment herein described. Such additions are preferably made after the resin has been carried through my process and the undesired volatile constituents have been eliminated.

In its dry soluble form it is best suited for use in varnishes and cellulose lacquers.

What I claim is—

1. The herein described method which comprises cooling a sludge-like synthetic resinous mass to produce a grindable substantially solid mass, then grinding the cooled mass into small particles, and then maintaining said particles in motion while subjecting the same to the drying action of an air current until the resinous particles are non-cohering.

2. The herein described method which comprises cooling a relatively wet sludge-like synthetic resinous mass to a temperature at which it can be mechanically ground, and below which the ground particles will agglomerate, then grinding the mass into small particles, and then maintaining the particles in motion while removing volatile substances therefrom.

3. The herein described method which comprises cooling and powdering a wet synthetic resinous mass, then maintaining the

particles of the mass in motion to prevent agglomeration, while simultaneously removing volatile substances therefrom.

4. The herein described method which comprises cooling and grinding a wet synthetic resinous mass, and then dehydrating the same while keeping the particles of the mass in motion at a temperature below their fusion point.

5. The herein described method which comprises cooling a wet synthetic resinous mass to a grindable condition, then grinding said mass to a fine powdery condition, then dehydrating the powdered mass with a current of moving gas so directed as to prevent the particles of the resin from coming to rest until the desired amount of volatile substances have been removed from the mass.

6. The herein described method which comprises cooling a wet synthetic resinous mass to a hard, grindable condition, then grinding the mass to a powdered condition, and then subjecting the powdered mass to air currents to maintain the particles of the mass in motion to prevent agglomeration of the same and to remove the volatile substances from the mass.

Signed at Philadelphia, in the county of Philadelphia and State of Pennsylvania, this ninth day of March, A. D. 1928.

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