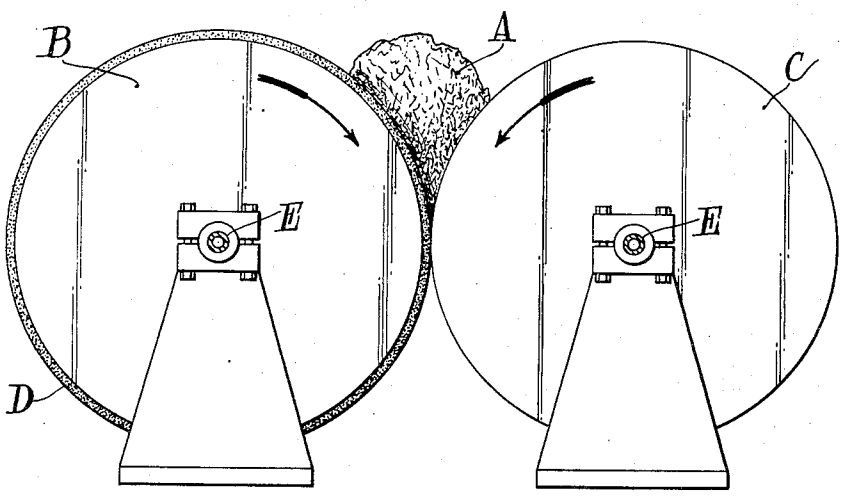
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MOLDING PROCESS

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MOLDING PROCESS

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This invention relates to the manufacture of plastic products and more particularly to the manufacture of colloidized or molded products, such as sheets, granules, powders and the like, from cellulose organic ester compositions, particularly those having a basis of cellulose acetate.

It is well known that many different compositions and many different processes have been employed in the production of cellulose ester plastics. One of the most widely employed methods is to flow a viscous solution of the cellulosic material in suitable solvents onto an appropriate surface and then cause the solvents to be evaporated, thereby casting the material into the desired form. Another method is simply to mix the cellulosic material in a relatively finely divided form together with a predetermined amount of solvent and/or plasticizer into a thick paste and extrude this through an opening of the desired shape.

In these and many other types of plastic processes a variety of cellulose derivatives have been employed, the best known and most widely used being cellulose nitrate and cellulose acetate, although various other inorganic and organic single and mixed esters, as well as ethers of cellulose have also been applied with more or less success. In the preparation of plastic compositions of this nature great emphasis has been placed, and rightly so, not only upon the type of cellulose compound itself, but especially upon the solvent and plasticizer employed. Much research work has been carried out and a great deal of literature published relating to these cellulose compounds, but notwithstanding this large accumulation of knowledge, especially with respect to the organic esters of cellulose typified by cellulose acetate, it is surprising that one of the most important facts concerning the use of this material in molding processes has previously been overlooked, namely, that the moisture content of the cellulosic material is of extreme importance and that it has a profound influence upon such important properties of the finished product as density, toughness, resiliency, tensile strength, shrinkage, warping, stability and resistance to chemical decomposition.

In working with cellulose ester plastics, I have discovered this quite inobvious and unexpected phenomenon and, in fact, have discovered that the moisture content of the cellulosic material is a critical factor and that by keeping it below a certain maximum a plastic product of greatly improved properties may be produced. This involved, not merely first drying the organic ester, but the discovery of the manner by which the moisture content of the ester could be reduced below a certain percentage and then working the ester up into a commercial product.

Although, for convenience of discussion and illustration, I shall describe my invention and its application with particular reference to cellulose acetate plastics, my process is equally applicable to the production of improved plastic products from any of the various cellulose organic esters.

The present invention has as an object to provide an improved technique for the manufacture of cellulose organic ester plastic products. A further object is to provide a process wherein a cellulose organic ester plastic may be produced which has markedly improved density, tensile strength, toughness, resistance to chemical action, improved stability, and other desirable properties. A still further and specific object of the invention is to produce an improved cellulose acetate plastic having the specific properties just enumerated. Other objects will hereinafter appear.

Cellulose ester plastic processes may, for convenience of illustration, be divided into two principal classes. The first of these includes processes wherein the plastic material is worked up into a plastic mass with the aid of solvents of a more or less volatile character. In such processes plasticizing substances, dyes, pigments or other coloring material are usually also added. Under this class may be included, for convenience, the method of plasticizing cellulose esters which comprises making a solution of the plasticizer in a liquid, such as benzol, which dissolves the plasticizer but which is a non-solvent for the cellulose ester and then treating (as by soaking and/or refluxing) the cellulose ester with such non-solvent solution so that the plasticizer thoroughly permeates the cellulose ester and then driving off the non-solvent, leaving the plasticizer behind thoroughly permeating the cellulose ester particles. The plasticized celluose ester may then be worked up on hot rolls and/or molded in known manner.

The second class includes those processes in which substantially no volatile solvents are employed, the cellulose ester material merely being worked up with the plasticizer and other ingredients which it may be desired to incorporate. The second type of process has the very great advantage that the resulting products have no volatile materials included in their structure which have to be removed, as is the case with products

produced according to the first mentioned class, by extensive curing operations. It is with the second class of molding processes that we are concerned in the present application, and most properly so for the reason that cellulose organic ester molded products of this type seem to have had no considerable commercial success in this country until my discovery of the critical element—low moisture content—which makes such products possible of useful commercial application.

In working with many different types of plastic processes in which a wide variety of cellulose ester materials were treated, I found that molded products produced from a cellulose ester material, such as cellulose acetate which has been air-dried in the usual manner and which contains from 2 to 6% of moisture, were subject to severe shrinkage and warping upon being removed from the mold. During processing it was also found that there was considerable swelling and puffing up of the material and that considerable quantities of gas or vapor were evolved from gas pockets formed within the plastic mass during the working-up process. Extensive experiments were carried out to discover the cause of these defects and it was found that they were due to the presence in the original cellulose ester of an appreciable amount of moisture. In addition to marked shrinkage and the presence of gas pockets, it was found that a plastic produced from high moisture cellulose ester material also had low density as well as low tensile strength and toughness. Microscopic examination of the internal structure showed that the greater the amount of moisture present in the material, the more spongy was its appearance, but that if the moisture was kept below .5%, a beautiful, lustrous product of exceptionally high density, high tensile strength, and low shrinkage and warp was produced.

I have determined that commercial cellulose acetate, for example, as ordinarily produced in precipitated form and oven-dried in ordinary heated atmospheric air, contains a relatively high percentage of moisture, generally in the vicinity of 2 to 6% and that a relatively high moisture content is, in varying degrees, characteristic of all air-dried cellulose ester material. In fact, it has been found that no matter how long one subjects the ordinary commercial cellulose acetate or other organic ester to air-drying at a non-decomposing temperature, one is unable to bring the moisture content down to a point lower than about 2%. I have found that even if oven-drying be continued for days beyond that ordinarily thought sufficient, the moisture content of the cellulose ester will not fall appreciably below 2%. Apparently there is occluded moisture in the cellulose acetate which it is impossible to remove by continued oven-drying, even of a relatively severe character. Accordingly, air-dried or oven-dried cellulose acetate or other esters referred to in the prior art may be regarded as containing upwards of 2% of moisture.

As indicated above, my invention may be said to comprise a dry molding process in which the moisture content of the cellulose ester plastic material is controlled within certain limits, resulting in the production of an improved plastic product. The steps of the process will be apparent from the following description of a typical molding process for the production of a cellulose acetate plastic, it being understood that the process described constitutes merely one of the preferred embodiments of the invention without in any sense being a limitation thereof.

The moisture content of the acetate before actually entering the molding operation is first reduced to the desired degree. I have discovered that the moisture can be brought down to less than .5%, only by converting the ester to a finely divided form to break up any agglomerates which tend to occlude moisture and then drying the finely divided material. In order to obtain the degree of fineness of particles desired I may, for example, grind the cellulose ester material in a ball mill or other suitable type of grinding or disintegrating machinery until it will pass a screen of given mesh. Another method of obtaining the material in finely divided form is to place it in solution and reprecipitate it therefrom by means of a mixture of solvent and non-solvent in accordance with the process disclosed in the copending application of D. E. Northrup and A. W. Crane, Serial No. 551,508, filed July 17, 1931, now U. S. Patent No. 1,991,115. The material produced by this latter method is particularly desirable, since its particles are of an open, porous, granular structure which, with or without additional comminution—as may be necessary, lend themselves especially well to treatment in accordance with the herein described process.

In the above paragraph, I have referred to finely divided material. This is to be understood as a somewhat relative expression and includes material of varying grades of fineness from that passing a screen of 40 mesh or below, say, even in some cases 20 mesh, to that passing 80 mesh or higher, say, even 160 mesh or more. However, as a general rule it may be said that the critical moisture content is more readily obtained with the finer grades of material. It may also be said that more satisfactory results are obtained if the particle size is kept relatively uniform. For example, it is preferable when using a 40–80 mesh material that no agglomerates incapable of passing a 40 mesh screen find their way into the mass and that all of the particles be as nearly as possible of the 40–80 mesh size, it being readily understood that large agglomerates diffuse in the molding mass less readily than do the smaller particles and thus produce a product of less uniformity.

Drying of the material in accordance with my invention is carried out by spreading the acetate in pan driers through which warm dry air is circulated at a low velocity. If drying is carried on for about 24 hours, the moisture content of the material in the case of 40–80 mesh material is reduced to approximately .5% or less. If the drying is carried on over a longer period of time say, for example, six days the moisture content is reduced to about .35%, while further drying for an additional period of nine or ten days brings the moisture content down to approximately .33%. My experiments have indicated that the moisture content should not run appreciably over .5% as a maximum, while the more satisfactory results are obtained with moisture content of below .5%, the best results being obtained at about .3 to .4%.

It should be noted at this point that if the cellulose acetate has been stored in the open for any considerable period of time, it should be resubjected to the drying treatment before use, as it has an inherent tendency to absorb moisture to the extent of 2 to 6%, depending upon atmospheric conditions and the type and form of pack-

age in which it has been stored, as well as the length of time of storage.

The actual molding mass is prepared by mixing together an appropriate amount of the cellulose ester material, plasticizer, and any other addition such as dyes, pigments, pearl essence, fillers and the like which may be desired, the use of volatile materials being avoided. The plasticizer and other materials added to the cellulose ester must, of course, be substantially anhydrous in order not to introduce undesirable moisture into the final plastic mass. The mass is then subjected to kneading on heated rolls as shown in the attached diagrammatic elevational drawing in which the mass A is kneaded between the heated and driven hollow rolls or drums B and C until entirely homogeneous. Both rolls may be driven, or only roll B. Heat is supplied to the rolls by means of steam, water or oil, as well known with such apparatus. I have found, for instance, the heat from about 40# to 150# steam works well. The heating fluid is introduced through pipes E suitably journaled or packed in the end of the drums B and C, which drums are mounted on the usual bearings. One of the drums (preferably the idler drum, if only one is driven) is on an adjustable axis so that the gap through which the material must pass, may be varied to correspondingly vary the pressure applied to the material during the kneading operation. I have found that with the drums rotating only a few R. P. M. that a 15 to 20 pound batch of plastic may be thoroughly kneaded and converted to a completely homogeneous mass in about five minutes. The kneading may be facilitated by occasionally pulling portions of the sheet D from the roll and throwing or twisting it over upon itself. With pigmented (including pearl essence) sheets, striated or streamed effects may be obtained in this manner. Striated, streamed or cascaded effects, particularly with pearl essence, may further be obtained by working the mass on the rolls to substantial homogeneity and then dropping here and there upon the rolls (where they converge) cubes or granules of previously prepared cellulose ester-pearl essence plastic in which the pearl essence is of relatively high concentration. These cubes or granules are preferably of the same cellulose ester as already upon the rolls. As the mass is further worked, the concentrated pearl essence is distributed in a beautiful heterogeneous pattern throughout the sheet D.

The hot plasticized sheet D is then stripped from the roll B and directly worked up into the desired form as soon as it leaves the kneading rolls, such as by pressing it further upon a hot platen press or in a mold, or it may be cut up into strips for molding desired shapes, or it may be cooled and broken up or granulated into small particles which in turn may be remolded in much the same manner as molding powders are molded. The granular material thus produced is a particularly valuable form of molding composition. Each of its granules is a sealed agglomerate of smaller particles homogeneously welded together into a unit. As the moisture has already been reduced to a substantially negligible minimum, and the plasticizer and cellulose ester are thoroughly colloidized by the combined action of heat and pressure on the calendar rolls, there results a colloidized material effectively sealed against the inter-penetration or absorption of moisture. It will be seen that the material is thus protected against deterioration and, since sufficient moisture does not collect on the surface of the granule to adversely affect its use in molding, these moisture-free granules are accordingly always ready for immediate use and, on recolloidizing in a suitable mold by heat and pressure, actually give a stronger product than results from molding the acetate powder-plasticizer mixture direct, by a single colloidization.

Attention is again called to the fact that the herein described process for the production of the plasticized cellulose ester material is characterized by comparative simplicity and that the material contains neither low boiling solvents nor moisture. It will thus be seen that the resulting product need not be cured or subjected to any other treatment before being used for the purpose for which it is ultimately intended.

With respect to plasticizing material, I have found that a wide variety of such agents may be employed so long as they are added to the cellulose ester in substantially anhydrous form. However, I have also found that tripropionin gives the most satisfactory results especially with dry cellulose acetate. The amount of this plasticizer which is employed may vary widely depending upon the degree of plasticity desired, as well as upon the working conditions of the process. I have found, for example, that from about 28 to 65 parts, or even more, of tripropionin per 100 parts of dry cellulose acetate is satisfactory. It may be said that this plasticizer is distinctive in several respects. For example, it has no appreciably rapid solvent action upon the cellulose ester in the cold and can, therefore, be readily mixed with the finely divided ester material without balling up, yet upon application of heat it readily colloidizes the material. This makes possible thorough incorporation of the plasticizer prior to the application of heat to the mass on the rolls. Tripropionin appears to have an almost unlimited plasticizing action on cellulose esters under heat and pressure. I have found it is not ordinarily necessary to change the plasticizing roll temperature with a change in the plasticizer content, as is the case with plasticizers, such as dimethyl phthalate, which have a higher solvent action on cellulose acetate.

While tripropionin is outstanding in its valuable properties, other plasticizers for cellulose acetate may be employed in my process. Among these may be mentioned dimethyl phthalate, penta-erythritol-tetracetate, triphenyl phosphate, tricresyl phosphate, monochlornaphthalene, triacetin, monoacetin. In addition to the plasticizers just mentioned, it has been found that diaceto glyceryl propionate, dipropionyl glyceryl acetate and dipropionin are good plasticizing materials for cellulose acetate. Their general plasticizing action for cellulose organic esters is more particularly referred to in the co-pending application of David C. Hull, Serial No. 665,335, filed of even date, and forms no part of the present invention, except that I have discovered that when cellulose acetate molding compositions are plasticized with propionyl-containing fatty acid esters of glycerine, highly satisfactory results may be obtained. In general, it may be said that the particular plasticizer employed with any given cellulose organic ester material will depend largely upon the particular cellulose ester dealt with, although I have found the foregoing propionic esters of especial value with cellulose organic esters.

The following example will serve to illustrate a typical dry molding process according to the invention.

Example

Cellulose acetate produced in accordance with

any of the known methods of making this material is ground in a conventional type of ball mill, preferably employing one-inch porcelain balls. The ground material is then screened and that portion passing an 80-mesh screen is spread upon trays to dry in a slow current of dry air. The drying is carried out for a period of time depending upon the amount of moisture it is desired to remove. The material is first subjected to a temperature of 150 F. for a period of 24 hours. This reduces the moisture content to approximately .5%. After this preliminary drying the material is further subjected to a period ranging from 1 to 6 days whereby the moisture is reduced to about .35%.

The thoroughly dried material containing in any case less than about .5% moisture is mixed with the plasticizer in the following manner: 100 parts by weight of the dried cellulose acetate is mixed with 28 parts by weight of substantially anhydrous tripropionin in a proper receptacle. The mixture is then transferred to kneading rolls where it is worked up and the plasticizer thoroughly incorporated at a temperature of about 300 to 320° F. although this temperature may vary (depending upon the ester, the plasticizer and proportion thereof) between that furnished by about 40# and 150# of steam, if desired. After thorough working up on the kneading rolls, the plastic mass may be passed to calender rolls for further calendering into thin sheets or it may be directly transferred into molds or onto platen presses for putting it into the desired form. Or the product may be crushed or granulated to any desired size such as ¼ to 1/64 inch approximate diameter and used for molding objects in the usual mold.

A product so produced will not shrink or warp upon cooling and standing and is unusually tough and strong. It is also a product of unusual density, an average of samples ranging in density from about 1.25 to about 1.56. With a higher proportion of plasticizer, the density of the product will vary slightly, decreasing with increased proportions of plasticizer.

If a colored product is desired, dyes, pigments, iridescent materials, such as pearl essence, bronze powder and the like, may be incorporated into the material at any desired point in the process. Dyes, for example, may be incorporated by simply working them into the plastic mass on the kneading rolls or by adding them to the mixture of cellulose ester and plasticizer before it is placed on the rolls. One particularly satisfactory method is to dissolve the dye in the plasticizer (of course, selecting a dye which is soluble in the plasticizer employed) and then incorporating the dyed plasticizer into the ester. This latter method is the subject of a co-pending application in the name of R. O. Wood, Serial No. 582,886 filed December 23, 1931, now U. S. Patent No. 1,966,327.

It will be seen from the above description that my plastic product is characterized by the complete absence of volatile solvents and the substantially complete absence of moisture. It therefore requires no further treatment, such as a curing operation, for removal of volatile constituents. More important, however, it is free from inclusion of moisture undesirably affecting its strength, density and other qualities as is inherently the case with prior art products produced in accordance with known methods and in which no effort has been made to reduce the moisture to a minimum as in the present invention.

As before alluded to, I have found that there is a rather definite relation between moisture and such properties as shrinkage, warping, tensile strength, toughness, density and the like. Shrinkage and warping increase, while toughness, tensile strength, and density decrease sharply when the moisture content increases about .5%. In fact a variety of curves might be plotted, illustrating the fact that these properties are functions of the moisture content.

While I have illustrated my invention by reference to cellulose acetate plastics, it is evident that it can be applied to dry molding processes in which various other cellulose organic esters, such as cellulose acetate propionate, cellulose acetate stearate, cellulose butyrate and other single and mixed esters of cellulose. As previously indicated an appropriate plasticizer will be employed, the particular plasticizer employed being largely a matter of selection and within the knowledge of the person skilled in the art. In general the operating conditions will be essentially the same with any of the higher cellulose esters and satisfactory products may be produced therefrom, providing, however, that the moisture content of the cellulosic material is brought down to the desired degree before the material is employed in the molding process. The material produced as above described is characterized by extreme toughness and resilience, this property rendering it especially adaptable for the manufacture of thin-walled articles. Photomicrographs of the material show that it is of an extremely dense and compact internal structure, free from gas pockets, bubbles or sponginess, which are common to molded products produced according to known methods. It is thermo-plastic, changing its physical form under heat and pressure without undergoing any chemical change. It has a beautiful lustrous finish and can be produced in any desired color, as indicated above, by the addition of pigments, dyes or other types of coloring material.

What I claim, and desire to be secured by Letters Patent of the United States is:

1. The process of making a cellulose organic ester plastic product which comprises first reducing the moisture content of the cellulose ester material to less than approximately .5%, incorporating a plasticizer therewith, and colloidizing the mixture under heat and pressure and in the substantial absence of volatile materials.

2. The process of making a cellulose organic ester plastic product which comprises first reducing the moisture content of the cellulose ester material to less than approximately .5%, incorporating a plasticizer therewith, colloidizing the mixture under heat and pressure and in the substantial absence of volatile materials, and molding the colloidized material in a condition in which it does not contain over approximately .5% moisture.

3. The process of making a cellulose organic ester plastic product which comprises first reducing the moisture content of the cellulose ester material to less than approximately .5%, incorporating a propionyl-containing ester of glycerine therewith, and colloidizing the mixture under heat and pressure and in the substantial absence of volatile materials.

4. The process of making a cellulose acetate plastic product which comprises first reducing the moisture content of the cellulose acetate to less than approximately .5%, incorporating a plasticizer therewith, and colloidizing the mixture under

heat and pressure and in the substantial absence of volatile materials.

5. The process of making a cellulose acetate plastic product which comprises first reducing the moisture content of the cellulose acetate to less than approximately .5%, incorporating a plasticizer therewith, and colloidizing the mixture under heat and pressure and in the substantial absence of volatile materials, and molding the colloidized material in a condition in which it does not contain over approximately .5% moisture.

6. The process of making a cellulose acetate plastic product which comprises first reducing the moisture content of the cellulose acetate to less than approximately .5% incorporating a propionyl-containing ester of glycerine therewith, and colloidizing the mixture under heat and pressure and in the substantial absence of volatile materials.

7. Colloidized cellulose organic ester molding material containing less than approximately .5% moisture and substantially no volatile materials.

8. Colloidized cellulose organic ester molding composition comprising a plasticizer and containing less than approximately .5% moisture and substantially no volatile materials.

9. Colloidized cellulose organic ester molding material plasticized with a propionyl-containing ester of glycerine and containing less than approximately .5% moisture and substantially no volatile materials.

10. Colloidized cellulose acetate molding material containing less than approximately .5% moisture and substantially no volatile materials.

11. Colloidized cellulose acetate molding material plasticized with a propionyl-containing ester of glycerine and containing less than approximately .5% moisture and substantially no volatile materials.

FRED R. CONKLIN.