United States Patent Office 3,485,652 Patented Dec. 23, 1969

3,485,652

MATTE FINISHED FORMED ARTICLE AND METHOD OF PRODUCING SAME

George P. Calloway, Jr., and Robert F. Williams, Jr., Rochester, N.Y., assignors to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey

No Drawing. Filed Aug. 4, 1967, Ser. No. 658,344
Int. Cl. C08b 21/06; C09j 3/04
U.S. Cl. 106—180 19 Claims

ABSTRACT OF THE DISCLOSURE

The present invention provides formed articles consisting essentially of blends of cellulose esters comprising from about 20% to about 80% of an amorphous, non-crystalline, geometrically irregular cellulose ester and from about 80% to about 20% of a crystalline, geometrically regular cellulose ester, which articles acquire a matte finish when they are solvent vapor treated. There is further provided a method of manufacturing matte finished formed articles comprising the step of solvent vapor treating formed articles of the above-described cellulose ester blends.

The present invention relates to matte finished formed articles consisting essentially of blends of geometrically irregular and geometrically regular cellulose esters and to a method for producing the same.

With the recently renewed emphasis on automobile safety, a demand has arisen for materials suitable for use in automobile trim and apparatus such as dashboards, switches, knobs and steering wheels, which materials provide little or no light reflection and provide increased hold or friction in applications such as steering wheels and switches. The search for such materials has naturally gravitated to thermoplastics such as the cellulose esters which, while the yare tough, are readily adaptable to any number of trim and apparatus utilizations due to their relatively low cost and ease of manufacture. In particular, it has been sought to produce, by abrasion or other means, matte-finished articles for use in automotive application such as those set out above wherein reduced reflection and increased hold are of substantial importance.

Similarly, numerous other applications such as desk tops and wallboard etc., where reduction of natural or artificial light reflection is of prime importance, demand the utilization of relatively low cost matte-finished formed thermoplastic materials which are decorative while at the same time functional.

It is therefore the object of the present invention to provide matte-finished formed thermoplastic articles, as well as a simplified and economic method of producing the same.

The present invention, in its generic article aspect, provides formed articles of manufacture consisting essentially of blends of cellulose esters comprising from about 20% to about 80% of an amorphous, non-crystalline, geometrically-irregular cellulose ester and from about 80% to about 20% of a crystalline, geometrically regular cellulose ester which formed articles acquire a matte finish when subjected to a solvent vapor treatment as described hereinafter.

We have discovered that formed articles of the special blends of cellulose esters, as above described, unexpectedly acquire a matte finish when subjected to a solvent vapor treatment commonly referred to as "vapor polishing." "Vapor polishing" is conventionally used to produce highly polished surfaces on formed articles of conventional cellulose esters. Such polishing techniques are presently utilized in the finishing of, for example, steering wheels, and the adaptability of the cellulose ester compositions of the present invention to such techniques should be of prime importance in producing matte-finished steering wheels having increased hold and, hence, greater safety.

Accordingly, the invention in its most generic process aspect provides a process for the manufacture of matte-finished formed articles such as steering wheels. This process comprises the step of solvent vapor treating a formed article consisting essentially of a blend of (a) from about 20% to about 80% of an amorphous, non-crystalline, geometrically irregular cellulose ester; and (b) from about 20% to about 80% of a crystalline, geometrically regular cellulose ester.

More specifically, the formed article is composed essentially of a blend of two types of cellulose esters, each ranging from about 20% to about 80% by weight of the finished article, and preferably having acyl substituents ranging from 2 to 4 carbon atoms.

THE NON-CRYSTALLINE CELLULOSE ESTERS

The amorphous, non-crystalline, geometrically irregular cellulose esters which are useful in our invention are generally those cellulose esters which do not readily crystallize to any practical degree when subjected to conventional thermoplastic molding or casting techniques (primarily due to their geometrical irregularity). These esters are generally characterized by one or both of the following two characteristics: (a) they have a minimum of 1% free hydroxyl, and they are either homogeneous esters, i.e. esters having a single type of acyl substituent, or mixed esters, i.e. esters having more than one type of acyl substituent; or (b) they are mixed cellulose esters whose ester substituents differ in composition by more than one carbon atom (for example cellulose acetate butyrate). Those skilled in the cellulose ester art will readily recognize the above two categories of cellulose esters as those which do not readily crystallize to any practical degree under conventional casting or molding conditions.

Such esters may be produced according to any conventional method. In the case of the cellulose acetates the esterifying liquid is made up primarily of acetic anhydride, acetic acid and sulfuric acid catalyst. In the case of cellulose acetate butyrate the esterifying liquid may be made up either of butyric anhydride, acetic acid and sulfuric acid catalyst or of acetic anhydride, butyric acid, and sulfuric acid catalyst depending on whether a high or low butyryl ester is desired. The proportion of catalyst employed in the esterification may be from 1.5 to 10% of sulfuric acid based on the dry weight of the cellulose. Ordinarily, to obtain esters of good viscosity the esterification temperature is not allowed to rise above 100° F. although the esterification temperatures employed depend somewhat upon the amount of sulfuric acid catalyst used, the more catalyst present in the esterification mass, the more important it becomes that the temperature of the reaction mass be carefully controlled. In order to terminate the esterification, water, ordinarily in the form of aqueous acetic acid, is added to the reaction mass in a sufficient proportion to convert the residual acetic anhydride to acetic acid. Also added to the mass either in this addition or in the aqueous acid which may be added to initiate the hydrolysis is a neutralizing agent which combines with a considerable proportion of the sulfuric acid to form a salt which is insoluble in the reaction mixture. Magnesia or magnesium compounds of weak acids i.e. magnesium carbonate have been found to be especially useful for this purpose as the magnesium sulfate formed is insoluble in the reaction mass. Since hydrolysis is desired, the greater portion of the catalyst which is present is neutralized and the hydrolysis is carried out but the

combined sulfuric acid in the final ester is thereby held to a sulfur content of .02–.001%.

In carrying out the hydrolysis of the cellulose ester the water in the form of aqueous acid which is added to the mass should be added at such a rate that it is uniformly worked into the hydrolysis mixture. Also, the addition and the hydrolysis should be at a temperature within the range of 110–180° F. After the ester has been hydrolyzed to the desired extent which is ordinarily to impart more than 1% free hydroxyl the ester is precipitated by the addition of aqueous acid to recover the ester. The ester is then given a thorough washing in water, preferably several washes with water having a low mineral content, such as less than 20 p.p.m. such as distilled water or Permutit-treated water.

Alternatively, cellulose butyrates suitable for use in the present invention may be produced according to the method disclosed in copending U.S. application Ser. No. 635,225 filed May 1, 1967. According to this process, toluene soluble cellulose butyrates may be prepared by heating a mixture of (*a*) cellulose butyrate containing at least about 52% butyryl, 0–1.5% acetyl, at most 0.25% hydroxyl, and at most about 0.006% sulfur as combined sulfate and (*b*) at most about 30% of free water, based on the weight of the liquids in the hydrolysis bath, dissolved in a solvent system consisting essentially of butyric acid at a temperature of from about 75° F. to about 300° F. until the percent hydroxyl of said cellulose butyrate is increased to within the range of from about 1% to about 3.2% hydroxyl, the mixture being substantially free of sulfuric acid and free fatty acid anhydrides.

The intrinsic viscosity of the amorphous, non-crystalline geometrically irregular esters must meet the same standard as that set out below for the geometrically regular esters, i.e. they must have an intrinsic viscosity greater than 1 in a methylene chloride-methyl alcohol solution (9:1).

GEOMETRICALLY REGULAR CELLULOSE ESTERS

The geometrically regular cellulose ester compositions which are crystalline in the formed articles of the present invention are the substantially fully esterified cellulose esters, in which at least ⅓ of the combined acyl is composed of fatty acid radicals having 3 to 4 carbon atoms, which esters contain at most about 0.5% hydroxyl and have an intrinsic viscosity of at least 1, after heating for one half hour at 250° C., in methylene chloride-methyl alcohol solution (9:1). In the case of mixed esters, 95% of the acyl groups therein should be the acyls which do not differ from each other by more than 1 carbon atom. Thus, esters useful in this member of the final blends of the present invention include cellulose tripropionate, cellulose tributyrate, cellulose propionate butyrate and cellulose acetate propionate having at most 20% acetyl content, all of which must have at most 0.5% free hydroxyl.

Examples of useful geometrically regular cellulose esters are those prepared by the procedure described in U.S. Patent 3,047,561 or those prepared by esterification procedures in which zinc chloride or some other non-combining (non-sulfur imparting) catalyst such as methane-trisulfonic acid or the like is employed. It is, of course, understood that the cellulose ester as it is prepared is not subjected to sufficient hydrolysis to increase its hydroxyl content beyond that specified herein. Esters which have the intrinsic viscosity prescribed herein are those prepared as described and preferably stabilized by a stabilization treatment such as disclosed in U.S. Patents 2,899,316 of Rouse and Hill, and 2,899,315 of Williams and Lowe, or a similar stabilization procedure. Suitable stabilizers include potassium acid oxalate, strontium naphthenate and p-tert-butyl phenol.

The cellulose ester blend may be produced by simply

blending one of each of the above-described cellulose ester compositions, as for example, by mixing on a rubber roll mill, or by any other convenient manner which results in the formation of a homogeneous blend of the special ester components.

The cellulose esters of our process and articles may be homogeneously mixed with suitable plasticizing materials in amounts up to 25% based on the cellulose esters. Some plasticizers suitable for use in this invention are triethyleneglycol di-2-ethylhexoate, triethylene-glycol di-2-ethyl-isohexoate, dibutyl sebacate, octyl adipates, dibutyl azelate and di(2-ethylhexyl) azelate.

Other materials which do not affect the product adversely may also be incorporated. For example, molding or casting aids such as paraffins may be incorporated to 1%, and dyes, fillers and extenders may be included to achieve the degree of color, toughness and flexibility which is desired in the particular application for which the formed article is destined.

The solvent vapor treatment which yields a highly polished surface when an article formed of a conventional cellulose ester composition is subjected thereto, and in the present process surprisingly yields a matte-finished article, is carried out according to conventional manipulative procedures, using the special ester compositions of this invention. Generally, such techniques involve suspending the formed article into concentrated organic solvent vapors over a typical degreasing-type of bath. The equipment for such a process is well known in the art, and consists of an upright tank-type of structure being open or openable at its top and having a reservoir of solvent at its bottom, which reservoir contains a quantity of solvent heated to just bleow, at, or just above its boiling point, the entire apparatus generally being open to the atmosphere and hence, subject to atmospheric pressure. The solvent vapors can be prevented from pouring over the sides of the bath by one condensing means or another. The conventional means is a circumferential lip about the inside of the tank at about ½ the depth thereof and which contains circulating cold water. Alternatively, a cold air blast which is likewise applied circumferentially at approximately ½ to ⅔ the depth of the tank may be utilized as the condensing means. The formed article to be treated is preferably suspended into the concentrated solvent vapors at a point below the condensing means and above the solvent reservoir so that the solvent vapors condense upon the formed article and then, when sufficient condensation has occurred, run off in the form of condensed solvent to fall back into the heated solvent reservoir. During the time at which the article being treated remains suspended in the solvent vapor (which may range from 2 to 3 seconds to several minutes depending upon the nature of the composition of the formed article, and of the solvent and the degree of matte which is sought to be imparted to the finish) the condensation of the solvent and its subsequent washing of the formed article surface causes a very small portion of the surface to be dissolved and washed away with the condensed solvent. It appears that it is the amorphous portions of the cellulose ester blends which, due to their more rapid rate of dissolution in the solvent, are washed away fastest, leaving the extremely desirable matte surface. It should be noted at this point that the formed article must be substantially cooler (i.e. at least about 5° C. cooler) than the temperature of the vapors when the article is placed in the solvent so that some of the solvent vapors can be condensed thereon.

Suitable solvents for the vapor treatment are known to those in the art and apparently any solvent that can be used to "vapor polish" articles made from conventional cellulose ester compositions can be used to produce the matte surfaced article of this invention. The preferred solvents include, trichloroethylene, butylacetate, methylacetate, ethylacetate, benzene and chlorinated solvents such as chloroform and methylene chloride. Trichloro-

ethylene is further preferred for optimum results since it is not flammable as are most of the other suitable solvents.

Subsequent to the solvent vapor treatment, the matte-finished formed article is preferably cured to remove any residual solvents by heating to a temperature just above the normal boiling point of the solvent, but substantially below the melting point of the formed article. Should the boiling point of the solvent approach the melting point of the formed article, the solvent vapor treatment and subsequent curing may be carried out in a vacuum in order to achieve a lower boiling point for the solvent.

The formed article may be produced by injection molding, casting or shaping the article according to any other conventional thermoplastic shaping means, several of which are commonly known to those skilled in the thermoplastic molding and casting arts.

The completed matte-finished formed article may be generally characterized as an article consisting essentially of crystalline and geometrically regular cellulose ester molecules having geometrically irregular and consequently amorphous cellulose ester molecules interspersed therebetween, the exact character of the article being dependent upon the ratio of crystalline to non-crystalline molecules present in the article.

The finished formed article of this invention is further generally characterized by having the ability to produce X-ray diffraction patterns characteristic of cellulose esters that contain a substantial proportion of crystalline ester.

Furthermore, articles having a matte-finish which demonstrate such characteristic X-ray diffraction patterns may be finally identified as the materials of this invention by subjecting them to the solvent vapor treatment described hereinabove. The formed articles of the present invention, wlli retain their matte finish and may become even rougher depending upon the nature of the particular composition, while articles of other cellulose esters compositions, such as those formed with blends of amorphous esters and rendered matte finished by abrasion or other means will acquire a smooth, and in some cases highly polished finish when subjected to the above-described solvent vapor treatment.

Our invention will be further illustrated by the following example:

EXAMPLE I

Bars ¼" by ½" by 5" are injection molded from an ester blend composed of 36.3% cellulose tri-propionate esters having 0.1% free hydroxyl, 54.6% cellulose acetate propionate esters, 2.2% acetyl and 45.7% propionyl, having 2.1% free hydroxyl and 9.1% dibutyl sebacate as plasticizer, and from a composition of 90.9% of the 2.1% free hydroxyl cellulose acetate propionate esters and 9.1% of the same plasticizer by injection molding from a screw type molding machine whose cylinder temperature was 450° F. into a heated mold. The mold temperature was 260° F. for the ester blend and 120° F. for the cellulose acetate propionate.

When the bars molded from the composition containing the mixture of the triester and hydrolyzed ester are suspended for five seconds in the vapors above a trichloroethylene bath heated to 86° C. a matte or dull finish is developed on the bars. They are then cured at 90° C. in an air circulating oven for a period of 20 minutes in order to remove any residual solvent present on or in the article.

When bars molded from the composition which contains no triester are subjected to the same treatment, high gloss surfaces develop.

The actual low gloss, matte finish of the article surface produced by the preferential attack of the solvent on the amorphous ester is thought to consist of either a series of extended fibers of the crystalline ester which have the amorphous material removed from between them, or alternatively, a surface which is crazed due to micro rendering caused by the same preferential attack of the solvent on the amorphous ester surface.

Since many changes and modifications can be made in the above-described details without departing from the nature and spirit of the invention, it is to be understood that the invention is not limited to said deails except as set forth in the appended claims.

We claim:

1. A formed article of manufacture consisting essentially of a blend of cellulose esters having acyl substituents of 2 to 4 carbon atoms, said blend comprising from about 20% to about 80% of an amorphous, non-crystalline, geometrically irregular cellulose ester and from about 20% to about 80% of a crystalline, geometrically regular cellulose ester, said formed article acquiring a matte finish when subjected to a solvent vapor treatment.

2. The formed article of manufacture of claim 1 wherein said amorphous, non-crystalline, geometrically irregular cellulose ester is a cellulose ester having an intrinsic viscosity greater than 1 in a methylene chloride-methyl alcohol solution (9:1) and is selected from the group consisting of (*a*) cellulose esters having a minimum of 1.0% free hydroxyl, and (*b*) mixed cellulose esters whose ester substituents differ in composition by more than 1 carbon atom.

3. The formed article of manufacture of claim 2 wherein said amorphous, non-crystalline, geometrically irregular cellulose ester is selected from the group consisting of cellulose acetate propionate having a minimum of 1% free hydroxyl, cellulose acetate butyrate, and cellulose propionate-butyrate having a minimum of 1.0% free hydroxyl.

4. The formed article of manufacture of claim 2 wherein said crystalline geometrically regular cellulose ester comprises a cellulose ester at least ⅓ of the combined acyl of which is made up of radicals of 3 to 4 carbon atom fatty acids in which 95% of the total acyl radicals differ from each other by no more than 1 carbon atom, which ester has at most 0.5% free hydroxyl and an intrinsic viscosity greater than 1 in a methylene chloride-methyl alcohol solution (9:1) even when the ester has been heated for one-half hour at 250° C.

5. The formed article of manufacture of claim 4 wherein said crystalline, geometrically regular cellulose ester is selected from the group consisting of cellulose acetate propionate having at most 20% acetyl and a maximum of 0.5% free hydroxyl, cellulose propionate butyrate having a maximum of 0.5% free hydroxyl, cellulose tripropionate having at most 0.5% free hydroxyl and cellulose tributyrate having a maximum of 0.5% free hydroxyl.

6. The formed article of manufacture of claim 4 wherein said blend of cellulose esters includes a stabilizer selected from the group consisting of potassium acid oxalate, strontium naphthenate and p-tert-butyl phenol.

7. The formed article of manufacture of claim 4 wherein said blend of cellulose esters includes up to 25% of a plasticizer selected from the group consisting of triethyleneglycol di - 2 - ethylhexoate, triethyleneglycol di - 2 - ethylisohexoate, dibutyl sebacate, octyl adipates, dibutyl azelate and di(2-ethylhexyl) azelate.

8. A process for the manufacture of a matte finished formed article comprising the step of solvent vapor treating a formed article comprising a blend of:

(A) from about 20% to about 80% of an amorphous, non-crystalline, geometrically irregular cellulose ester having acyl substituents of 2 to 4 carbon atoms; and

(B) from about 20% to about 80% of a crystalline, geometrically regular cellulose ester having acyl substituents of 2 to 4 carbon atoms.

9. A process for the manufacture of a matte finished formed article in accordance with claim 8 wherein said solvent vapor treating is accomplished by suspending said formed article in solvent vapors such that said solvent vapors condense upon said formed article and dur-

ing subsequent run-off wash the surface of said formed article.

10. A process for the manufacture of a matte finished formed article in accordance with claim **9** wherein said solvent vapor consists essentially of vapor of a solvent selected from the group consisting of trichloroethylene, methyl acetate, ethyl acetate, butyl acetate, benzene, chloroform and methylene chloride.

11. A process for the manufacture of a matte finished formed article in accordance with claim **9** wherein said amorphous geometrically irregular cellulose ester has an intrinsic viscosity greater than 1 in a methylene chloride-methylalcohol solution (9:1) and is selected from the group consisting of (*a*) cellulose esters having a minimum of 1% free hydroxyl, and (*b*) mixed cellulose esters whose substituents differ in composition by more than 1 carbon atom.

12. A process for the manufacture of a matte finished formed article in accordance with claim **11** wherein said amorphous, geometrically irregular cellulose ester is selected from the group consisting of cellulose acetate-propionate having a minimum of 1% free hydroxyl, cellulose acetate-butyrate, and cellulose propionate-butyrate having a minimum of 1.0% free hydroxyl.

13. A process for the manufacture of a matte finished formed article in accordance with claim **11** wherein said geometrically regular cellulose ester comprises a cellulose ester at least ⅓ of the combined acyl of which is made up of radicals of 3 to 4 carbon atom fatty acids in which 95% of the total acyl radicals differ from each other by at most 1 carbon atom, which ester has at most 0.5% free hydroxyl and an intrinsic viscosity greater than 1 in a methylene chloride-methyl alcohol solution (9:1) even when the ester has been heated for one-half hour at 250° C.

14. A process for the manufacture of a matte finished formed article in accordance with claim **13** wherein said geometrically regular cellulose ester is selected from the group consisting of cellulose acetate propionate having at most 20% acetyl and at most 0.5% free hydroxyl, cellulose propionate butyrate having at most 0.5% free hydroxyl, cellulose tripropionate having at most 0.5% free hydroxyl, and cellulose tributyrate having at most 0.5% free hydroxyl.

15. A process for the manufacture of a matte finished formed article in accordance with claim **13** wherein said blend includes a stabilizer selected from the group consisting of potassium acid oxalate, strontium naphthenate and p-tert-butylphenol.

16. A process for the manufacture of a matte finished formed article in accordance with claim **13** wherein said blend includes up to 25% of a plasticizer selected from the group consisting of triethyleneglycol di-2-ethyl-hexoate, dibutyl sebacate, octyl adipates, dibutyl azelate and di(2-ethylhexyl) azelate.

17. A process for the manufacture of a matte finished formed article in accordance with claim **13** wherein said blend of A and B is formed by mixing components A and B on a rubber roll mill and said formed article is produced by injection molding.

18. A process for the manufacture of matte finished formed articles in accordance with claim **13** wherein subsequent to said solvent vapor treating, said formed article is heated at atmospheric pressure to a temperature above the boiling point of the solvent utilized in said solvent vapor treating and below the melting point of said formed article in order to remove residual solvents present upon or within the article.

19. A process for the manufacture of a matte finished formed article in accordance with claim **13** wherein said solvent vapor treating is accomplished by suspending said formed article in the vapors above a trichloroethylene bath heated to about 86° C. for a period of above five seconds, and said formed article is subsequently cured by heating to 90° C. for a period of from one to twenty minutes.

References Cited

UNITED STATES PATENTS

1,774,184	8/1930	Palmer et al.	106—192
1,838,121	12/1931	Vles	106—192
1,920,212	8/1933	Payne et al.	106—192
2,052,590	9/1936	Whitehead	106—192
3,020,661	2/1962	Miller et al.	264—341

MORRIS LIEBMAN, Primary Examiner

H. H. FLETCHER, Assistant Examiner

U.S. Cl. X.R.

106—169, 178, 181, 189, 190, 191, 192, 198; 264—344

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,485,652 Dated December 23, 1969

Inventor(s) George P. Calloway, Jr. and Robert F. Williams, Jr.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 38 "the yare" should read --they are--.
Column 6, line 4, "deails" should read --details--.
Column 8, line 9, between "hexoate" and "dibutyl" insert --triethyleneglycol di-2-ethylisohexoate--.

SIGNED AND
SEALED
JUN 30 1970

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents