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MOLDED PRODUCT

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This invention relates to molded products in which an attractive color effect is produced by the incorporation of a small amount of a metallic powder. The invention includes both the new products and their manufacture.

The molded products of this invention glisten and reflect the light in such a way as to resemble a pearly material and produce what has become known in the art as a pearlescent effect. The light is reflected unevenly. Portions of the surface appear light in color and these lighter portions are separated by areas, usually irregular lines of material, which appear darker in contrast. The glistening effect is much like that in pearls although the breaking up of the light into its various colors and the play of the colors of the rainbow on the surface is less evident than in pearls and in most instances is entirely absent.

According to this invention a small amount of a metallic powder is incorporated in a thermoplastic material, which when molded in thin layers is transparent or translucent, the metallic powder being substantially evenly distributed throughout the plastic material. The mixture in lump or powder or other suitable form is placed in a mold and subjected to high pressure at an elevated temperature. It is found that the molded product thus produced exhibits the pearlescent effect above described.

In carrying out this invention various metallic powders may be employed such as aluminum powder, copper and aluminum bronzes, powdered magnesium, lead and zinc, etc. The powder may be somewhat flaked and in general improved results are thus obtained although the pearlescent effect has been produced by powders which are not flaked. The size of the metallic powder employed may vary although in general the finer the powder the more satisfactory the product obtained. Usually it is preferable to employ metallic powders of a size such that all of the powder will pass through a 150-mesh screen and preferably a powder substantially all of which will pass through a 250- or 300-mesh screen, since when powders containing coarser material are employed, fine particles of the metal are observable on the surface of the molded product.

The amount of metal employed will vary but in general from $\frac{1}{10}$ of one part to one part in 100 parts by weight of the thermoplastic material gives the most satisfactory results. It will, of course, be understood that the desirable amount will depend somewhat upon the specific gravity of the metallic powder employed. Thus, one part of powdered aluminum per 100 parts of plastic material will not give quite as satisfactory a result for most purposes as somewhat less than one part. On the other hand, with heavier metals such as bronzes, an amount in the neighborhood of one part or somewhat more gives very

pleasing results. In general, however, between $\frac{1}{10}$ of a part and one part of a powdered metal, substantially all of which will pass through a 250- or 300-mesh screen gives the most satisfactory results. Somewhat more than one part of powdered metal may be employed although in most cases as much as 5% of powdered metal appreciably reduces the pearlescent effect. Using small amounts of powder, even less than $\frac{1}{10}$ of a part per 100 parts of the molding material, products may be formed which are substantially transparent, but yet exhibit the pearlescent effect when viewed by reflected light.

The most prominent pearlescent effect is produced with transparent or substantially transparent thermoplastics. A thermoplastic which is not entirely transparent may be employed and in certain instances it is desirable to add to the thermoplastic a material which will tend to mask the pearlescent effect and produce a somewhat smoky iridescent surface. Polymerized vinyl chloride known as "vinylite", styrol plastic compounds and cellulose plastic compounds, such as nitrocellulose and cellulose acetate may be employed in producing the molded compounds of this invention. The preferred embodiment of the invention, however, consists of molded products made from rubber derivatives and, particularly, the rubber derivative prepared by first treating rubber with hydrochloric acid and the halide of an amphoteric metal or preferably chlorostannic acid and then breaking down the tin addition compound thus obtained as described below.

By incorporating metallic powders in these plastic materials, various color effects may be produced. Using bronze powders, a golden or brownish product having the desired pearlescent effect is obtained. A mixture of a bronze powder with aluminum powder produces a somewhat different and also attractive effect. Soluble dyes may be added to the plastic material in addition to the metallic powders to give pearlescent products of substantially any color. In fact, when the metallic powder is light in color, as for example aluminum or magnesium powder, the use of some dyestuff which is soluble in the plastic material will usually be found desirable.

The following procedure may be followed to produce the pearlescent effect in molded products made from rubber derivatives.

A rubber cement is prepared by dissolving 10 parts by weight of plasticized pale crepe rubber in 100 parts of benzene. The rubber is plasticized on a mill until a sample measuring $\frac{1}{16}$ of an inch in each direction when placed on a flat plate beneath a flat 10 kilogram weight for $3\frac{1}{2}$ minutes in a cabinet heated to a temperature of 70° C. is flattened out to a thickness slightly less than $\frac{1}{8}$ inch. This corresponds to a plasticity in the neighborhood of 300 as determined by the

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Williams plastometer. The molding properties of the rubber derivative produced may be varied somewhat by using rubber which has been plasticized to a somewhat different extent.

- 5 350 gallons of the rubber cement so prepared is placed in a steam jacketed Day mixer equipped with a reflux condenser and approximately 10% of hydrated chlorostannic acid, based on the weight of the rubber in the cement, is added.
- 10 The chlorostannic acid is conveniently prepared by adding sufficient aqueous hydrochloric acid to tin chloride to provide the water required for the six molecules of water of hydration and then hydrogen chloride gas is passed through the resulting solution at room temperature until the chlorostannic acid is produced. The mixture of cement and chlorostannic acid is heated and agitated for a period of three hours at a temperature near the boiling point of the solvent and preferably between 65 and 80° C. After heating for this time the reaction mixture is sampled every few minutes and the viscosity determined. Heating for an additional three hours or more may be required to produce a product of the viscosity desired. When the desired viscosity has been obtained, the reaction is terminated either by adding water or an alkali.

To determine the viscosity one may employ a Gardner mobilometer, an instrument measuring the viscosity of a sample in terms of the time in minutes required for a plunger of known weight and area to fall a known distance in a cylinder of known volume containing a test sample. The clearance between the plunger and the wall of the cylinder is also known. It is preferable to take all readings at one temperature and 25° C. is selected for testing the samples referred to herein. The viscosities referred to below were determined in a mobilometer having the following dimensions:

Thickness of plunger disc-----	0.066	inches
Diameter of plunger disc-----	1.502	do
Diameter of plunger shaft-----	0.248	do
Inside diameter of cylinder containing test sample-----	1.535	do
Play of cylinder-----	9.0	do
Length of plunger shaft-----	20.0	do
Distance between the two marks on the plunger shaft-----	7.484	do
Total weight of shaft, top weight and disc-----	68.6	grams

- When the viscosity of the cement tests 0.10 to 0.30 minute or somewhat higher or lower, as desired, the reaction is terminated by the addition of alkali to neutralize the reaction mixture, (for example 40 grams of sodium hydroxide dissolved in water, per pound of chlorostannic acid used) or by dilution with water (as by the addition of one-half pound of water per pound of chlorostannic acid used). The batch is then cooled and filtered. The reacted cement is then discharged into somewhat more than its own volume of water (for example, about 2½ gallons of water for each gallon of reacted cement) at ordinary room temperature and agitated by a propeller rotating at approximately 240 R. P. M. ¾ of an ounce of sodium sulfite or other reducing agent per gallon of water may be added to the water employed for quenching to prevent oxidation of the reaction product.

It appears that during the reaction of the chlorostannic acid on the rubber tin combines in some way with the rubber and that afterwards it is split off when the reaction mixture is

quenched in water. The product obtained on quenching contains chlorine and appears to be a hydrogen chloride addition product having a $(C_5H_5)_x$ nucleus in which more carbon atoms are directly connected than in rubber. It is a condensation derivative of rubber. Using the halide of an amphoteric metal without hydrochloric acid, for example, stannic chloride, aluminum chloride, chromic chloride and the like condensation derivatives of rubber are obtained which in purified form appear to be a hydrocarbon having the empirical formula $(C_5H_5)_x$ in which more carbon atoms are directly connected than in rubber.

The benzene is removed from the emulsion obtained on quenching, preferably by steam distillation. For example, steam is introduced at such a rate that the vapor temperature in an ordinary column extending from the reactor to a condenser reaches 154° F. in 40 minutes. During the next 30 minutes the temperature is maintained at 154° F., during which interval the majority of the solvent distills over into a condenser. The temperature is then increased to 210° F. during the next 50 minutes and kept there for an additional 25 minutes during which practically all of the remainder of the solvent distills off. By such distillation of the solvent the rubber derivative is precipitated in a finely divided sand-like form. It is then centrifuged, washed with water and dried in a vacuum oven.

The production of the rubber derivative may be varied considerably from the method here outlined and the above example is given merely as illustrating one method of producing a product desirable for molding. This product molds readily at temperatures in the neighborhood of from 240° F. to 300° F. and higher using pressures of 1000 pounds per square inch or more. The time required for molding will vary with the temperature and pressure employed and also with the shape of the molded product. Derivatives of different viscosities are best molded under different temperature and pressure conditions. If a higher temperature than necessary is employed there is a tendency to cause an excess of flow across the surface of the mold which decreases the pearlescent effect.

The metallic powder to be used for producing the pearlescent effect is advantageously milled into the rubber derivative on mill rollers such as a rubber mill, where sufficient heat is generated to soften the derivative to a point where the powder may be finely distributed throughout the rubber derivative. As milling tends to flatten the metal particles and thus increase the amount of light reflected from each particle this is the preferred method of incorporating the metal in the molding material. Soluble dyestuffs, where employed, may also advantageously be added to the derivative on a rubber mill and the dyes and powder may advantageously be worked into the derivative in the same milling operation. In general, any oil soluble dyestuff will dissolve in the rubber derivative.

The derivative with the metallic powder evenly distributed throughout it is then cooled and ground to a desired fineness. The area of the glistening portions of the final product bounded by the dark lines depends largely upon the size of the particles of the derivative filled into the mold. On molding, the particles of the derivative are flattened out and occupy a somewhat greater area than when in ground form. In molding a flat piece where there is no vertical

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flow, the finer the particle size the smaller the pearlescent areas produced. Particles the size of grains of sand produce a fine pearlescent effect. Particles retained on a $\frac{1}{8}$ inch screen

5 produce a pearlescent effect with larger glistening areas than produced by smaller particles. A mixture of particles of different sizes, such as that obtained by grinding without sieving produces a pleasing pearlescent effect.

10 The following examples are illustrative of formulae of molding material produced on a rubber mill, using rubber derivative produced as above described.

Example 1

	Parts by weight
Rubber derivative (.25 viscosity) -----	100
Antique copper bronze powder -----	0.5

Example 2

	Parts by weight
Rubber derivative (.25 viscosity) -----	100
Oil soluble red dye -----	0.05
Aluminum powder -----	0.10

Example 3

	Parts by weight
Rubber derivative (.18 viscosity) -----	100
Copper bronze powder -----	1

Example 4

	Parts by weight
Rubber derivative (.30 viscosity) -----	100
Copper bronze powder -----	0.5
Aluminum powder -----	0.25

Example 5

	Parts by weight
Rubber derivative (.18 viscosity) -----	100
Aluminum powder -----	0.25
Oil soluble blue dye -----	0.05

40 The red dye used in Example 2 is xylo-azo-xylo-azo-beta-naphthol. The blue dye used in Example 5 is 1-methyl-amino-4-para-tolyl-amino-anthraquinone. A pleasing effect was also obtained using .05 part aluminum, .50 part #15

45 fire bronze of the Ohio Bronze Powder Company and .10 part of an oil soluble black dye. Omitting the dye and using .25 part aluminum and .50 part #15 fire bronze also gave a good pearlescent effect. The metallic powders used were

50 those commercially available. The aluminum powder was coated with a lubricant, stearic acid (probably $\frac{1}{2}$ to 3%), but the use of stearic acid or other lubricant appears unnecessary.

To produce a transparent product which exhibits the pearlescent effect when viewed by reflected light a small amount of metallic powder is added. The particles are so small as to have little or no effect on the transparency of the material if used in small amount. A minimum

60 amount of flat leaf-like particles is preferred for this purpose. The finer the particles, the lower the weight of metal required. One-half part of a copper powder 95% of which passes through a 200-mesh screen and 100% of which passes

65 through a 170-mesh screen will give a transparent product if a transparent molding material is used. As little as 0.01 part of a fine aluminum powder 99.5% of which passes through a 250-mesh screen and 100% of which passes

70 through a 200-mesh screen milled into the rubber derivative on a mill gives the pearlescent effect with little decrease in transparency. As little as 0.05 part of aluminum of this size milled into the rubber derivative decreases the transparency materially. 0.15 part of copper 99.5%

of which passes through a 250-mesh screen and all of which passes through a 200-mesh screen, if milled into the rubber derivative, gives a transparent pearlescent product on molding. The transparency is materially reduced by using 0.25

5 part of copper powder of this size. Such transparent products may be colored by the addition of a soluble dye.

By milling very fine metal powders into transparent molding materials such as cellulose acetate, cellulose nitrate and vinylite a molding material is produced which on molding at minimum temperature produces transparent products which exhibit the pearlescent effect when viewed by reflected light.

In molding these compositions the temperature employed has been found to alter the pearlescent effect produced. The pearlescent effect appears to be due to the reflection of light from the metallic surfaces. It appears that in the molding operation, as pressure is applied and the molding material flows and fills the mold, the metal particles are brought into alignment in the plane in which the material flows, which is a plane approximately parallel to the surface

25 of the mold. By lubricating the surfaces of the particles, as by coating them with stearic acid, better alignment is obtained. As the pearlescent effect is produced by the reflection of light from the metal surfaces, a more intense effect is produced by flat leaf-like particles than the same weight of particles of other shape. By working the mixture of molding material and metal particles on a mill the particles may be flattened. In milling the powder into the thermoplastic material on a mill it is advantageous to add the powder gradually and spread it over the entire width of the roll in order to prevent a high concentration of the metal in one spot which would tend to cause the fine powder to agglomerate into

35 larger particles.

If the molding material is heated during molding to a point where it becomes too soft there is less alignment or no alignment of the particles and the most pronounced pearlescent effect is obtained by molding at the lowest molding temperature. In Examples 1 and 2 a pleasing pearlescent effect is produced on flat pieces with little vertical flow by using a pressure of 1000 to 2000 pounds per square inch and a temperature of 240-250° F. In molding a material of the viscosity shown in Examples 3 and 5, using pressures of 1000 to 2000 pounds a temperature of 260-275° F. is preferred. With a material with a viscosity of .30, as in Example 4 a temperature as low as 225° F. may advantageously be used.

If a less prominent pearlescent effect is desired the temperature used for molding may be increased. In certain cases it may be desirable to load the plastic material with a toner such as titanium oxide to give a lighter colored product. Usually from 0.5 to 2.0 parts by weight on 100 parts of the rubber derivative gives satisfactory results. The following example illustrates this procedure.

	Parts
Rubber derivative -----	100
Canary toner X786 -----	0.10
(Imperial Color Works)	
Powdered aluminum -----	0.50
TiO ₂ -----	0.50
Red dye (same as used in Example 2) -----	0.10

More than 2 parts by weight of titanium oxide masks the pearlescent effect to such an extent that it is scarcely discernible.

The rubber derivatives after molding may be advantageously dipped in chlorine water to increase their resistance to oils and greases, and may otherwise be treated as desired.

5 As a further example of thermoplastic materials which may be used in molding products having the pearlescent effect of this invention, the following is suggested.

10 100 parts by weight of "vinylite" (a polymerized vinyl compound) which was translucent or transparent and 0.5 part of blue dye were mixed on a mill heated to 160° F., sufficient vinylite being used to form a bank on the mill. Approximately 0.06 part of aluminum bronze were introduced 15 into the bite of the mill and thoroughly mixed by cutting the vinylite composition and rolling it and repassing it through the mill several times. The product was molded with heat and pressure. A pleasing pearlescent effect was produced in the 20 resulting molded product.

Treating cellulose acetate or cellulose nitrate in the same manner gives a desirable pearlescent effect. Other dyes and other metallic powders may be used and the proportions varied to produce the effect desired.

25 In molding the compositions of this invention, somewhat different effects are produced in different molds depending upon the shape of the mold employed. For example, in molding tumblers 30 from the thermoplastic rubber derivative described above the pearlescent effect produced on the bottom of the tumbler may be that of fine scales or flakes and on the walls of the tumbler the pearlescent areas may be somewhat extended 35 in the direction of the height of the tumbler.

The pearlescent effect may be enhanced by the use of soap in the molding operation. The soap may be milled into the rubber derivative; it may be used in liquid form to coat particles of the 40 derivative before molding or a powdered soap such as zinc stearate may be dusted over the molding material before introducing it into the mold; or the mold may be brushed with a liquid soap before it is used for molding. For example, 45 2 parts by weight of castile soap chips milled into a molding mixture of 100 parts of the rubber derivative, 0.25 part of powdered aluminum, and 0.05 part of the blue dye used in Example 5 was found to give a somewhat more pronounced 50 pearlescent effect than that obtained with the formula of Example 5. Liquid potassium soaps, coconut oil soap, ivory soap chips and ivory soap solutions have been used and found to increase the pearlescent effect. The soap appears 55 to break up the smooth flow and give the desirable pearlescent, wavy, depth-of-surface appearance which is characteristic of these products. Even where products requiring small flow are molded, the addition of a small amount of soap to the formulae given above often enhances the pearlescent effect and generally improves the molding properties of the rubber derivative. Other 60 lubricants such as carnauba wax or carnauba wax in benzol may be used instead of soap for lubricating the mold, etc.

This application is in part a continuation of application Serial No. 655,678, filed February 7, 1933.

It is intended that the patent shall cover, by suitable expression in the appended claims, whatever features of patentable novelty reside in the 70 invention.

What we claim is:

1. The step in the method of producing a molded product which comprises milling between 0.1 75 and 1.0 part by weight of a metallic powder into

100 parts by weight of the rubber derivative formed by first treating rubber with hydrochloric acid and the halide of an amphoteric metal and then splitting off tin from the resulting product to produce a thermoplastic material, a thin layer 5 of which when molded will produce a transparent or translucent product.

2. The method of forming molded products having a pearlescent effect which comprises milling 10 metallic particles into thermoplastic material (a thin molded layer of which is transparent or translucent) so as to obtain a substantially uniform distribution thereof in the thermoplastic material, subdividing the resulting product into 15 lumps of suitable size for molding, filling the resulting lumps into a mold and molding therein with heat under pressure.

3. The method of forming molded products having a pearlescent surface composed of a plurality of light-reflecting areas separated by darker 20 zones, which comprises milling a metallic powder in a molding material (a thin molded layer of which is transparent or translucent), grinding the resulting mass, supplying resulting particles of subdivided material in sizes at least as large 25 as grains of sand to a mold and subjecting it to heat and pressure therein.

4. The method of forming a molded product with a surface composed of light-reflecting areas separated by darker zones which comprises supplying 30 to a mold particles of subdivided molding material in sizes at least as large as grains of sand (a thin molded layer of which molding material is transparent or translucent) which molding 35 material has small light-reflecting particles distributed throughout it, and subjecting the molding material to heat and pressure in the mold to cause it to flow therein and fill the mold and thus form a molded product with a surface composed of light reflecting areas separated by 40 darker zones.

5. A molded product which comprises small light-reflecting particles distributed throughout a molding material (a thin molded layer of which 45 is transparent or translucent) and at the surface of said molded product light-reflecting areas separated by darker lines or areas, the small light-reflecting particles in the light-reflecting areas being so oriented as to cause markedly greater light-reflection therefrom than from the 50 darker lines or areas.

6. The process of claim 4 in which the molding material is a condensation derivative of rubber.

7. The process of claim 4 in which the molding material is a cellulose derivative.

8. The process of claim 4 in which the molding material is cellulose acetate.

9. The process of claim 4 in which the molding material is a vinyl compound.

10. The product of claim 5 in which the molding material is a condensation derivative of rubber.

11. The product of claim 5 in which the molding material is a cellulose derivative.

12. The product of claim 5 in which the molding material is cellulose acetate.

13. The product of claim 5 in which the molding material is a vinyl compound.

14. The method of forming a molded product 70 with a surface composed of light-reflecting areas separated by darker zones which comprises milling a metallic powder into a molding material (a thin molded layer of which is transparent or translucent), subdividing the resulting product 75

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into particles at least the size of grains of sand, filling resulting particles into a mold and molding it therein with heat under pressure.

15. The method of forming molded products 5 which comprises distributing a powder of light-reflecting particles throughout a mass of a molding material (a thin molded layer of which is transparent or translucent) and dyeing said molding material with a soluble dyestuff, subdividing the resulting product into particles at 10 least the size of grains of sand, filling resulting particles into a mold and molding it therein with heat under pressure.

16. A dyed molded product which comprises 15 small light-reflecting particles distributed throughout a molding material (a thin molded layer of which is transparent or translucent), and on the surface of said molded product light-reflecting areas separated by darker zones, the 20 small light-reflecting particles in the light-reflecting areas being so oriented as to cause markedly greater light-reflection therefrom than from the darker lines or areas.

17. The method of forming a molded product a surface of which is composed of light-reflecting areas separated by darker zones which comprises pressing against a surface in a mold, a subdivided mass of molding material (a thin molded layer 5 of which is transparent or translucent), which mass comprises particles at least the size of grains of sand throughout which small light-reflecting particles are substantially evenly distributed.

18. A product with a molded surface composed 10 of light-reflecting areas separated by darker zones which surface is composed of a molding material (a thin molded layer of which is transparent or translucent) in which are small light-reflecting particles which are so oriented in the 15 light-reflecting areas as to cause markedly greater light reflection from these areas than from the darker zones.

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DISCLAIMER

2,054,454.—*Herman R. Thies* and *Theodore A. Riehl*, Akron, Ohio. MOLDED PRODUCT. Patent dated September 15, 1936. Disclaimer filed March 30, 1939, by the assignee, *Wingfoot Corporation*.

Hereby disclaims from product claims 5, 11, 12, 13, 16, and 18 all products embodying light reflecting particles other than metallic particles; and hereby disclaims from process claims 4, 6, 7, 8, 9, 10, 15, and 17 all processes using light reflecting particles other than metallic particles.

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