PATENT SPECIFICATION 596,233

Convention Date (United States of America): Feb. 19, 1944.

Application Date (in United Kingdom): Dec. 5, 1944. No. 24293/44.

Complete Specification Accepted: Dec. 31, 1947.

COMPLETE SPECIFICATION

Elastomer-Carbon Black Mix and Method of Making same

We, THE GENERAL TIRE & RUBBER COMPANY, a corporation organized under the laws of the State of Ohio, United States of America, 1708, Englewood Avenue, Akron, County of Summit, State of Ohio, United States of America, assignees of THEODORE ALCOTT TEGROTENHUIS and CHARLES BEDELL FROST, both citizens of the United States of America, of Columbia Road, Olmsted Falls, County of Cuyahoga, State of Ohio, United States of America, and Young Men's Christian Association, Akron, County of Summit, State of Ohio, United States of America, respectively, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to a method of making rubberlike articles reinforced with finely divided carbon, such for example as carbon black. It particularly relates to a process of compounding aqueous dispersions of rubbery polymerization products, wherein finely divided carbon is incorporated in aqueous rubber dispersions and the material coagulated and masticated.

It has heretofore been proposed to compound natural rubber or dispersions of synthetic rubbers, such as the rubbery copolymers of butadiene with styrene and with acrylonitrile, by incorporating in the latex or aqueous dispersions a suitable dispersion of carbon black and other compounding agents. The latex thus compounded may be utilized for the preparation of unmasticated rubberlike articles, such as dipped goods and the like. However, in such unmasticated rubbers, the carbon black serves merely as a filler and coloring medium.

For the preparation of articles reinforced by carbon black, it has heretofore been proposed to coagulate the latex-black mixture dry the coagulum thus obtained in the same manner as the rubbery polymer is dried in conventional practice and to masticate the dried coagulum thus obtained on a suitable mill or Banbury mixer to cause breakdown and plasticization of the rubber and intimate dispersion of the particles of the black throughout the mass thereof. The incorporation of the black in the latex permits much faster breakdown of the rubbery polymer when the dried coagulum is subjected to mastication.

One such previous proposal relates to the preparation of crumb-like solids from latex compounded with carbon black and it is stated that the crumb can either be placed on racks to dry or may be pressed through rollers, or placed in presses to squeeze out the bulk of the water; but there is no disclosure of the causing of plastic flow throughout the mass thereof, that is, throughout the mass of the individual particles to cause smearing of the black. Neither is there any disclosure of the desirability of such a process or the superiority of such a process over simple pressing or squeezing, which does not cause any plastic flow, but on the contrary drying, simple pressing and passage through squeeze rolls were regarded as equivalent. The object in that case was to produce a crumb for moulding and further processing, such crumb not being destroyed by squeezing without plastic flow, whereas plastic flow as brought about in the present invention does destroy this crumb. Another previous proposal discloses the washing of a mix containing synthetic rubber and carbon black but in that process any mastication or plastic flow would be in the presence of free water, which permits loss of black. No previous publications disclose the benefits to be derived from the plastic flow of a wet rubber-black mixture according to the process of the present invention.

The uniformity and degree of dispersion of the black in the rubber and the physical properties of the rubber articles produced are usually not as good as the conventional mill mixed rubber. This is believed to be due to the fact that addition of a coagulant to the compounded aqueous dispersion, in addition to causing agglomeration of the rubbery particles, also causes agglomeration of the pigment particles so that relatively large agglomerates of pigments are

dispersed within the rubbery mass. The dispersion of hard agglomerates in such a rubbery mass is very difficult and it is sometimes almost impossible to accomplish, probably because the breakdown of the rubber occurs so rapidly that the plasticity of the rubbery material is insufficient to shear the relatively hard black agglomerates.

To overcome the formation of these agglomerates, attempts have been made to improve the quality and stability of the pigment dispersion by use of relatively larger quantities of dispersing agent, such as long chain polyglycerides, sulfolignins, condensation products of formaldehydes and naphthalene sulfonic acids, tannins such as quebracho, and the like. While the use of larger quantities of these materials apparently acts to reduce the number of lumps or granules of visible pigment agglomerates below the number present when a carbon black slurry without dispersing agent or with smaller quantities of dispersing agent is used, the relatively smaller agglomerates apparently remain. This is evidenced by the fact that physical properties of the rubber produced are oftentimes inferior to those obtainable by the conventional mill mixing processes.

It is therefore an object of the present invention to provide a method of processing natural or artificial rubbery polymerization products wherein carbon black is incorporated in the latex prior to coagulation and mastication treatments. This method provides a rubber mix which, when vulcanized, has properties at least equivalent to those of rubbers prepared in conventional manner, wherein the dry black is incorporated in the solid mass of broken-down rubber in the mill or Banbury mixer.

It is another object of the present invention to provide a method of processing rubber or producing rubber articles wherein carbon black is incorporated in the aqueous dispersion of the rubbery polymer, and wherein completely mixed rubber batches are produced in but a fraction of the time and power required according to conventional mixing procedures.

It is a further object of the present invention to produce from compounded aqueous dispersions of rubber or rubberlike polymerization products articles having the rubber reinforced by finely divided carbon and having physical properties at least as desirable as those obtained by conventional mixing procedures.

It is a still further object of the present invention to produce rubber articles reinforced with finely divided carbon black wherein the carbon black is incorporated in the aqueous dispersion of rubberlike material and wherein a dispersing agent is not required.

We have found that these and other objects, as will be apparent from the following description of the invention, are accomplished by incorporating in any suitable way carbon black in an aqueous dispersion of rubberlike material to obtain a relatively uniform fluid mixture; coagulating the rubberlike material to entrap the carbon black in intimate mixture with the coagulum of rubberlike material; and then subjecting the coagulum while still retaining a substantial amount of moisture to a shear between relatively closely spaced surfaces which bear strongly against the coagulum. This shearing action is sufficient to cause plastic flow throughout the mass of the coagulum. It is obtainable by moving the coagulum relative to contacting and tightly pressing surfaces, as in the case of extrusion, or by passing the coagulum one or more times between closely set rolls which travel at different peripheral speeds.

The retention in the coagulum passed through squeeze rolls of a substantial amount of water, evidently greatly facilitates the breaking up of the fine invisible agglomerates as well as the relatively large particles of carbon black. Therefore, the rubber articles produced from the mixture obtained have properties at least equal to and generally superior to those obtained by the conventional mill mixing procedures. In addition, the mixtures may be produced with the required plasticity in as little as one-half the time required for conventional mill mixing.

According to the present invention, therefore, finely divided carbon black in amounts of at least 25% of the weight of the rubberlike material is combined with an aqueous dispersion of a rubberlike material to form a mixture, and solids of said mixture are coagulated together, separated from free, aqueous liquid, and in the absence of the free, aqueous liquid subjected to mechanical shear to cause flow throughout the mass thereof and smearing of the separate particles of rubber and carbon black, while the mass still contains above 1% by weight of moisture in relation to the content of rubberlike material, and preferably above 2% of the total of rubberlike material and black, which prevents the hardening of carbon black agglomerates prior to the smearing treatment.

The carbon black may be incorporated in the latex in any convenient way known to provide a relatively uniform mix. If dilution of the aqueous dispersion of rubber with relatively large quantities of

water is not undesirable, the black may be incorporated as an aqueous slurry without a dispersing agent, with or without previous colloid mill or equivalent treatment. If dilution of the latex or aqueous dispersion is to be kept at a minimum and the use of a dispersing agent in substantial quantities is not objectionable from the economic viewpoint, the black may be prepared in the form of a dispersion by passing a water-carbon-black slurry containing a dispersing agent through suitable dispersing apparatus to obtain a dispersion in accordance with conventional latex technology. If a dispersing agent is incorporated in the latex and if a powdered (non-beaded) black is utilized, the black may be simply stirred into the latex mixture and dispersed therethrough by stirring or other suitable agitation of the latex-black mix.

Coagulation of the relatively fluid latex-black mixture may be accomplished in any suitable manner, as by the addition of an electrolyte, such as a salt and/or acidic material. To facilitate washing, coagulation is preferably accomplished according to methods by which a crumb of moderate size is obtained. Thus, a crumb may be obtained, as is well know in the art, by adding a salt solution to the latexlike mixture in sufficient amount to render the mix unstable.

In the ordinary synthetic rubber plants, coagulation is accomplished by mixing the latex with a substantial quantity of salt solution under conditions of turbulence, and thereafter incorporating acidic material, such as sulfuric or acetic acid, to change soap to fatty acid. This method or any other method may be used in accordance with our process.

In accordance with conventional procedure, in the synthetic rubber industry, the coagulated rubber, which may be in either crumb or pelletlike form, is subjected to a drying operation to reduce moisture to a minimum value. Thus, the specifications of the rubber reserve GR—S plants in the United States require the drying of the rubbery polymer to an extent such that the maximum volatile matter present is .75% of the rubber. In practice, the moisture content (moisture capable of being driven off by heating below temperatures destructive to the rubbery hydrocarbon) is reduced much below this figure.

We have discovered that the ease of dispersion by mastication of carbon black in a coagulated mix of rubberlike material and black is related to the moisture content of the rubber-black mix. In accordance with the present invention, the rubber-black mixture is subjected to the aforementioned shearing or wet smearing operation while the moisture content is sufficient to permit dispersion of the particles of black by a few passes through mill rolls or the equivalent, as compared to the many passes heretofore required. The moisture content is at least 1% of the rubber content and preferably above 2% of the total of rubber and black. The shearing or smearing operation is most effective to cause dispersion of the black after coagulation and any time before the moisture content is reduced below 5% of the rubber. The coagulated solids of the relatively wet rubber-black mixture may be passed through suitable shearing rolls to cause plastic flow or working throughout the mass thereof as soon as possible after the washing water has been drained from their surfaces.

The shearing of the black in the rubber to cause disruption of the agglomerated pigment or to retain the pigment in dispersed form may be accomplished in a number of different ways. We have found, however, that at least one or two passes between rolls such as those of a rubber mill or calender, which rotate at different speeds, are most effective in disrupting the wet agglomerates. When the coagulum is sufficiently dry, smooth rolls may be provided. However, when the coagulum is relatively wet, rolls having a knurled or corrugated surface to compress the rubbery polymer into a sheet are desirable. A single pass through the relatively tight-fitting rolls is usually sufficient to provide the desired dispersion and to permit the attainment of properties commensurate with those of rubber produced by usual procedures. If desired, however, the crumb or coagulum may be dried to 2 to 10% moisture packaged or baled in the usual manner, and thereafter subjected to shearing action on a mill or Banbury mixer. This latter procedure permits the shearing step to be accomplished at great distances from the point where the aqueous dispersion of rubber and black is coagulated.

The aforementioned treatment is particularly applicable to the processing of synthetic rubbers, such as rubbery copolymers produced by polymerizing a material comprising a major proportion of butadiene and/or one or more conjugated dienes, preferably having six carbons or less, such as 2,3 dimethyl butadiene 1,3, chloroprene, 2,3 dichlorobutadiene 1,3, with a minor proportion of one or more polymer-forming materials, containing at least one polymerizable unsaturated group. Examples of such polymer-forming materials are styrene, acrylonitrile, acrylates, vinyl pyridine, dimethyl - vinyl - ethinyl - carbinol,

$(CH_3)_2C=CH-C\equiv C-CH_2OH$ (dm.v.e.c.), allyl chloride, methallyl chloride, and other unsaturated chlorides, or mixtures containing any one or more of these or equivalent materials in minor proportion. The process is also applicable to the polymers of butadiene, isoprene, chloroprene or rubbers containing a major proportion of one or more of these materials or other dienes which are polymerizable to rubbery polymers. It is also applicable to rubbers formed by condensation procedures, such as the olefine polysulphides and linear polyhydric alcohol-dibasic acid condensation products.

The term rubberlike materials as used in the specification includes these various synthetic rubbers mentioned above.

The following examples illustrate the present invention:

EXAMPLE 1.

45 parts of Carbon Black (W-6)
450 ,, ,, Water
400 ,, ,, 25% GR-S Latex

The carbon black and water were mixed together; the fluid and unstable mixture, while being retained under constant agitation to maintain distribution of the beaded black, was passed through a Charlotte-type colloid mill to obtain a relatively stable slurry. The slurry thus obtained was mixed with the latex and the mixture poured into a suitable coagulant, such as a highly agitated solution of salt and acetic acid, to coagulate the rubber in the form of crumbs having a maximum dimension of about one-eighth inch or so. The crumbs thus prepared were filtered and washed in relatively clean water for a period of one-half hour. The washed crumbs were thoroughly drained so that the moisture content was between 5 and 20%. The crumbs were then passed through corrugated rolls to form a thick sheet, which sheet was then passed once between rubber mill rolls which had different peripheral speeds and which were spaced about one-sixteenth inch or less apart to obtain a thin sheet. This thin sheet was then dried to about .5% of volatile matter. The dried rubber thus obtained was without any further mastication, except that required for the addition of curing agents, compounded according to a standard formula, cured for about fifty minutes at 287° F. The rubber obtained had a tensile strength of about 3,100 pounds per square inch and an elongation of about 600%. The rubber showed an entire absence of visible agglomerates, indicating a relatively good dispersion.

When in this example the crumbs were dried according to conventional procedures to meet GR—S specifications of less than .75% volatile matter and the mixture then compounded on a rubber mill to the same formula, the tensile strength of the cured rubber was only about 2,200 pounds per square inch and the rubber showed a very large number of visible agglomerates or pieces of black.

When in Example 1 the washed crumbs were dried to about 2% moisture, based on the rubbery polymer plus the black, and the mixture then mixed with curing agents in the usual manner, substantially the same results were obtained as indicated in Example 1. Like Example 1, the mixing and compounding was completed in but half the time required for conventional mixing procedures and great savings in power required were obtained. In addition, the compounded mixture processed much more readily than mixtures compounded in the conventional manner.

EXAMPLE 2.

45 parts of Carbon Black (W-6)
150 ,, ,, Water
400 ,, ,, 25% GR-S Latex
10 ,, ,, Dispersing Agent (Daxad (Registered Trade Mark)—condensation product of formaldehyde and naphthalene sulphonic acid).

The dispersion prepared by passing the black, water and dispersing agent through a colloid mill was stirred with the latex. The mixture thus obtained was coagulated to form a crumb, and the crumb washed with water, separated from the free-uncombined affluent and passed through squeeze rolls mechanically to shear the rubber carbon black coagulant and cause flow throughout the mass thereof. The coagulant thus treated was dried to about .5% of moisture and then compounded according to standard formula and cured as in Example 1. The tensile strength of the resultant rubber was about 2900 pounds per square inch and the cuts in the rubber showed no visible evidence of agglomerates.

When, as in the above example, the latex black mixture was coagulated, washed and dried, in accordance with conventional procedure, and the compound cured in exactly the same way, the resultant rubber had a tensile strength of only 1800 pounds per square inch and an elongation of about 600%. The freshly-cut surface showed few visible agglomerates, the number being somewhat less than when the mixture was formed without a dispersing agent in the carbon black slurry, other conditions and treatments being exactly the same, showing that the use of dispersing agent like the plastic flow throughout the wet, rubber black mix also contributes to the absence of agglo-

merates.

EXAMPLE 3.

45 parts of Carbon Black (W-6)
200 ,, ,, Water
400 ,, ,, 25% GR-S Latex
10 ,, ,, Dispersing Agent (Sodium Lignin Sulfonate)

The carbon black, water and dispersing agent were passed through the colloid mill and incorporated in the latex, as in Example 2. The rubber-black mixture thus obtained was coagulated, washed and dried as in Example 1 to about 5% moisture and then given our wet smearing treatment by compounding in a Banbury mixer. The tensile strength of the rubber produced was 2,900 pounds per square inch and the dispersion showed substantially entire absence of agglomerates.

The preparation of a slurry is facilitated when .5 part or other suitable amount of a wetting agent, such as one of those set forth in the list starting on page 127 of "Industrial and Engineering Chemistry," Vol. 35, No. 1, January, 1943, or in the list starting on page 17 of "Industrial and Engineering Chemistry," Vol. 33, No. 1, January, 1941, is incorporated in the water of Example 4 prior to formation of a carbon black-water slurry.

Any of the desired types of finely divided carbon, such lamp black, channel black, furnace black, or gas black, may be used in preparing the rubber compounds of the present invention. The amount of black used is preferably sufficient to cause improvement in properties of rubbery polymers, such improved properties being characterized by reinforcement, i.e., increase in tensile strength, stiffening of the polymer, and/or increased resistance of the rubbery material to abrasion. By the aforementioned moist or wet smearing or shearing action, superior dispersion and greater efficiency of the use of the black usually results.

In rubbery polymers such as the rubbery copolymers of butadiene with styrene or acrylonitrile or in natural rubber latices, the black usually amounts from 25 to 60 parts of black for each 100 parts of the rubbery material of the latex. Larger amounts may be used, however, and it is sometimes preferable to prepare the rubber-carbon black mixture in masterbatch form, containing say 100 parts or so of black for each 100 parts of rubberlike material, and thereafter mix therewith a suitable amount of rubbery material to obtain the desired black content.

The following example illustrates the above masterbatch procedure.

EXAMPLE 4.

110 parts of Carbon Black (Binney & Smith W-6 powder)
550 parts of Water
10 ,, ,, Purified Sodium Lignin Sulfonate
400 parts of 25% GR-S Latex

The above ingredients were mixed, coagulated, dried to 2—5% moisture content and given a shearing treatment by passing through mill rolls, all as in Example 1, to obtain a carbon black-GR-S masterbatch having the carbon black dispersed throughout the rubbery material. A separated batch of GR-S latex was mixed with the desired amounts of a dispersion of zinc oxide, sulfur and rubber softener and also coagulated, dried to 2—5% moisture. A sufficient amount of the carbon black masterbatch and other desired materials were then combined on a mill with the required amount of the other rubbery mix to give proportions corresponding to a standard test formula. The rubber after curing for fifty minutes at 287° F. had a tensile strength of about 3,200 pounds per square inch and an elongation of about 600%. A freshly cut surface of the rubber showed an entire absence of visible agglomerates.

The GR-S latex may be substituted by dispersions of other rubberlike materials, including natural rubber, rubbery polymers and copolymers, as aforementioned, mixtures of any one or more of these materials, dispersions of black within the rubber or polymer being produced with but a fraction of the power and time required for conventional mixing procedures.

Since the synthetic rubber-producing factories are located at substantial distances from rubber-processing factories where apparatus for subjecting the rubber-black mixture to a shearing treatment is available, it is frequently desirable in the practice of the present invention to simply dry or squeeze the rubber-black mixture to a moisture or volatile content above 2% and to bale or box the thus treated material for shipment to the processing factories.

By processing rubbers in accordance with the present invention, the output of the masticating machinery is increased from 30 to 60% and, in addition, the mixture has superior processing properties, particularly when the amount of black exceeds 25 or 30% of the rubbery polymer. Thus, the mixes produced in accordance with the present invention also have the advantage of tubing much more readily to form articles of the desired shape, such as treads and the like. In addition, the presence of moisture, as

aforementioned, seems to improve the curing properties of the rubbery material.

It is to be understood that variations and modifications of the specific processes herein shown and described for purposes of illustration may be made without departing from the spirit of the invention.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for compounding rubberlike material as herein defined wherein finely divided carbon in amounts of at least 25% by weight of the rubberlike material is mixed with an aqueous liquid dispersion of said rubberlike material, and solids of the mixture thus formed are coagulated together and drained of further liquid, characterised by the step which comprises subjecting the coagulated carbon-rubberlike material to a mechanised shearing treatment to cause plastic flow throughout the mass thereof and smearing of the particles of black and rubberlike material after separation of said coagulum from free liquid while the mass still contains at least 1% of moisture in relation to the content of rubberlike material and prior to reducing the liquid content of the mixture below 2% of the weight of the rubberlike material plus the carbon.

2. A process according to claim 1 in which the mechanised shearing treatment is carried out as claimed in claim 1 prior to reducing the liquid content of the mixture to between 1% and 2% by weight of moisture in relation to the content of rubberlike material.

3. A process for compounding rubberlike material as herein defined according to the preceding claims, characterized in that the rubberlike material used is selected from the group consisting of natural rubbers, rubbery polymers and copolymers of a material containing a major portion of a conjugated diene of less than seven carbon atoms.

4. A process for compounding rubberlike material as herein defined according to any of the preceding claims, characterized in that the mixture is subjected to said mechanical shearing treatment while the mixture contains 2% to 20% of moisture.

5. A process for compounding rubberlike material as herein defined according to any of the preceding claims, characterized in that the mechanical shearing treatment is effected while the liquid content is above 5% of the mixture.

6. A process for compounding rubberlike material as herein defined according to any of the preceding claims, further characterized in that the carbon black is prepared in the form of a slurry in aqueous liquid prior to its addition to the aqueous dispersion of rubberlike material and in that the shearing treatment comprises subjecting the wet coagulated carbon-rubberlike material mixture to shear deformation by moving it between and relatively to spaced surfaces which tightly bear against said material mixture to smear out agglomerated particles of carbon while wet.

7. A process for compounding rubberlike material as herein defined according to claim 6, further characterized in that the relatively moving surfaces are rolls having different peripheral speeds.

8. A process for compounding rubberlike material as herein defined according to any of the preceding claims, wherein the finely divided carbon is prepared in the form of an aqueous slurry having an absence of effective amounts of dispersing agent.

9. The process of making rubberlike material, as herein defined, reinforced with finely divided carbon substantially as described.

10. A rubberlike material as herein defined reinforced by finely divided carbon made in accordance with the process defined in any of the preceding claims.

Dated this 5th day of December, 1944.

MEWBURN, ELLIS & CO.,
70 & 72, Chancery Lane,
London, W.C.2,
Chartered Patent Agents.

Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press.—1948.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies, price 1s. 0d. each (inland) 1s. 1d. (abroad) may be obtained.

aforementioned, seems to improve the curing properties of the rubbery material.

It is to be understood that variations and modifications of the specific processes herein shown and described for purposes of illustration may be made without departing from the spirit of the invention.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for compounding rubberlike material as herein defined wherein finely divided carbon in amounts of at least 25% by weight of the rubberlike material is mixed with an aqueous liquid dispersion of said rubberlike material, and solids of the mixture thus formed are coagulated together and drained of further liquid, characterised by the step which comprises subjecting the coagulated carbon-rubberlike material to a mechanised shearing treatment to cause plastic flow throughout the mass thereof and smearing of the particles of black and rubberlike material after separation of said coagulum from free liquid while the mass still contains at least 1% of moisture in relation to the content of rubberlike material and prior to reducing the liquid content of the mixture below 2% of the weight of the rubberlike material plus the carbon.

2. A process according to claim 1 in which the mechanised shearing treatment is carried out as claimed in claim 1 prior to reducing the liquid content of the mixture to between 1% and 2% by weight of moisture in relation to the content of rubberlike material.

3. A process for compounding rubberlike material as herein defined according to the preceding claims, characterized in that the rubberlike material used is selected from the group consisting of natural rubbers, rubbery polymers and copolymers of a material containing a major portion of a conjugated diene of less than seven carbon atoms.

4. A process for compounding rubberlike material as herein defined according to any of the preceding claims, characterized in that the mixture is subjected to said mechanical shearing treatment while the mixture contains 2% to 20% of moisture.

5. A process for compounding rubberlike material as herein defined according to any of the preceding claims, characterized in that the mechanical shearing treatment is effected while the liquid content is above 5% of the mixture.

6. A process for compounding rubberlike material as herein defined according to any of the preceding claims, further characterized in that the carbon black is prepared in the form of a slurry in aqueous liquid prior to its addition to the aqueous dispersion of rubberlike material and in that the shearing treatment comprises subjecting the wet coagulated carbon-rubberlike material mixture to shear deformation by moving it between and relatively to spaced surfaces which tightly bear against said material mixture to smear out agglomerated particles of carbon while wet.

7. A process for compounding rubberlike material as herein defined according to claim 6, further characterized in that the relatively moving surfaces are rolls having different peripheral speeds.

8. A process for compounding rubberlike material as herein defined according to any of the preceding claims, wherein the finely divided carbon is prepared in the form of an aqueous slurry having an absence of effective amounts of dispersing agent.

9. The process of making rubberlike material, as herein defined, reinforced with finely divided carbon substantially as described.

10. A rubberlike material as herein defined reinforced by finely divided carbon made in accordance with the process defined in any of the preceding claims.

Dated this 5th day of December, 1944.

MEWBURN, ELLIS & CO.,
70 & 72, Chancery Lane,
London, W.C.2,
Chartered Patent Agents.

Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press.—1948.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies, price 1s. 0d. each (inland) 1s. 1d. (abroad) may be obtained.

* C L M S *

Mewburn Ellis