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Singapore

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Inventor:—FREDERICK WALTER SHIPLEY.

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COMPLETE SPECIFICATION

Improvements in or relating to the Production of Rubber Compositions

WE, THE BOARD OF THE RUBBER RESEARCH INSTITUTE OF MALAYA, a Body Corporate of Malaysia, of 3rd Mile Ampang Road, Kuala Lumpur, Malaya, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

- 10 This invention is for improvements in or relating to the production of rubber compositions and has for an object to provide a method of producing a masterbatch of natural rubber containing carbon black.
- 15 In the manufacture of many rubber goods it is necessary to mix carbon black into the rubber. Carbon black confers highly important reinforcing properties to the rubber vulcanisate. It has long been the practice to effect this mixing in the dry state by the use of heavy mixing machinery. Such machinery is costly and also the handling of the carbon black is itself objectionable as the finely divided material permeates the atmosphere and makes it almost impossible to maintain the surroundings and machinery clean and uncontaminated by carbon black. By the use of a ready-made mixture of carbon black and rubber (i.e. a so-called carbon black masterbatch), the latter difficulty is avoided and at the same time more economic use of the mixing equipment is rendered possible in that the time required to mix any given compound is substantially reduced.

The invention relates to the production of a carbon black masterbatch of natural rubber formed by the mixing of carbon black with rubber in latex form followed by the simultaneous coagulation together of rubber and carbon black.

Natural rubber latex is normally coagu-

lated by means of acid, a process usually taking several hours at least. Although it is possible to coagulate latex with acid in the presence of carbon black, it is very difficult to maintain a uniform distribution of the carbon black or so to adjust conditions that co-precipitation of both rubber and carbon black is complete. Moreover, these difficulties are increased by the thickening or flocculating action of carbon black itself on natural latex.

This invention is based upon our discovery that it is possible to utilise the flocculating effect of carbon black in order to produce a satisfactory masterbatch.

Carbon black is ordinarily supplied in the form of pellets and these are ground to a fine state of subdivision by passing through a grinder which is essentially a high-speed hammer mill and a machine suitable for this purpose is that which is sold under the proprietary name "Mikro-Pulverizer".

The finely divided carbon black is stirred into water containing a dispersing agent. Whilst various dispersing agents can be used, particularly satisfactory products are the sodium salt of methylene dinaphthalene sulphonate which is sold under the Trade Mark Dispersol LN and the sodium salt of a sulphonation product of lignin which is sold under the Trade Name Marasperse CB. The amount of dispersing agents used will vary with the nature of the carbon black but the amount is ordinarily from 1% to 2% based upon the weight of the carbon black. The dispersed carbon black is usually further reduced in size by passing the initial dispersion through a colloid mill; a single pass through a colloid mill is ordinarily adequate since repeated passes only increase the viscosity of the slurry and somewhat reduce its tendency to settle but have no other significant effect on

[Price 4s. 6d.]

the final properties of the product.

Various commonly employed carbon blacks can be employed including types of carbon black known as ISAF (intermediate

- 5 super abrasion furnace black) and SAF (super abrasion furnace black). The present invention is found to provide excellent masterbatches utilising these two carbon blacks which are especially difficult to
10 disperse by conventional means in ordinary oil-extended rubber stocks.

- According to the present invention there is provided a process for the manufacture of a natural rubber/carbon black masterbatch which comprises adding an aqueous dispersion of carbon black, stabilised with a dispersing agent, to a natural rubber field latex, optionally preserved by the use of up to 0.2% by weight of ammonia, agitating to effect uniform mixing of the carbon black dispersion in said latex and continuing agitation until the rubber flocculates and finally coagulates and thereafter separating the coagulum from the serum, the carbon
15 black being used in amounts up to 100% of the weight of the rubber in the latex. The rubber latex used is a field latex, i.e. a latex obtained directly from the rubber tree and delivered to the factory on or near
20 to the plantation for processing into various forms of rubber as normally marketed. Whilst the field latex can be used as such, it is often convenient to add small amounts, for example 0.1 to 0.2% by weight of the
25 latex, of ammonia, this addition having the effect of delaying the onset of putrefactive thickening.

- The invention is applicable to the production of natural rubber masterbatches in
40 which the rubber is extended with oil and accordingly it is a feature of the invention that an aqueous emulsion of a mineral oil containing an emulsifying agent is intimately admixed with the latex prior to the
45 admixture therewith of the carbon black. The emulsifying agent used is conveniently a soap such as a laurate or oleate of sodium, potassium or ammonia or tetra-ethylene pentamine acetate; in producing
50 the mineral oil emulsions, 0.4 to 1.0% of, for example, oleic acid is added to a mineral oil and this is stirred into water containing 0.1 to 0.3% of a base, such as ammonia, calculated on the weight of the
55 oil, the amount of water being approximately half the weight of oil. The initial coarse emulsion will be passed through an emulsifier in order to reduce the droplet size of the oil and this oil emulsion is then
60 mixed with the latex with gentle stirring.

- When operating batch-wise, especially on a large scale, it is preferred to delay slightly the onset of thickening by the addition of a small amount of protective
65 agent to the latex. Many of the usual

surface-active substances may be used for this purpose, a preferred material being a polyglycol known as Polyglycol HS 35/40. This is added, in aqueous solution, to the latex before the addition of the oil emulsion, about 0.1 to 0.2% based on the weight of the rubber being used.

The carbon black dispersion and the latex containing oil are mixed together and are then stirred very vigorously for about 1
75 minute. By this time thickening has set in and a further slow mixing for several minutes completes the coagulation. The serum is removed by simple filtration under gravity.

An alternative method of proceeding is to meter, in two separate continuous streams, in the desired ratio, the carbon black dispersion and the latex, which may contain oil, by means of two metering
85 pumps, into a totally enclosed mixer of construction described in the following. Two parallel shafts rotating at 500 to 800 r.p.m. (variable) have along about half their length a series of staggered projecting
90 pins that intermesh with a small clearance between each other and the casing. The two metered liquid streams enter the mixer through two perforated delivery tubes, the two emerging sprays facing and impinging
95 on each other between the rotating shafts. A pitched face to the pins helps to drive the mixture axially along the mixer during which time coagulation sets in and the viscosity increases rapidly. Beyond the
100 pins and also rotating on the shafts are two strongly pitched expellers which move the mixed mass along to the exit tube in the base of the mixer. The shafts rotate on ball bearings at each end, set in cast aluminium blocks, protected by oil seals.

The coagulum produced by either method (batch-wise or continuous) is filtered on a wire of nylon mesh filter to remove the serum, passed through a dicing or comminuting machine to reduce the crumb size and dried in warm air. Drying is completed in 2 to 3 days at 140°F. in gently moving air or in a few hours if dried in deep beds under forced draught.

The dried coagulum of the rubber masterbatch is conveniently baled into blocks in conventional manner. Upon
115 subjection to subsequent mixing in conventional rubber mastication and mixing
120 machinery the shear forces exerted on the masterbatch, even when containing large amounts of extending oil e.g. up to 70 parts per 100 parts of rubber, are such as to complete the dispersion of the carbon
125 black and to bring it to that state of subdivision and dispersion normally achieved by conventional procedures and which is necessary for the development of the optimum degree of physical properties. 130

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We find that it is possible to use the extender oil in amounts up to 70% by weight of the rubber in the latex.

The following Examples are given to illustrate the manner in which the invention may be carried into effect and the percentage figures quoted therein are calculated by weight unless otherwise stated.

Example I

Natural rubber field latex having a dry rubber content of 34.0% was protected by the addition of 0.1% ammonia (based on weight of latex) and 0.2% Polyglycol HS 35/40. A naphthenic mineral extending oil sold under the Trade Name Circosol 596 was emulsified with half its weight of water by means of ammonium oleate (0.5% oleic acid dissolved in the oil and 0.1% ammonia dissolved in the water). Carbon black of the type known as ISAF was passed once through a "Mikro-Pulverizer" (Trade Mark) and stirred into water containing 1.5% of the dispersing agent Marasperse CB and the resultant slurry passed once through a colloid mill with the plates set at a separation of 0.002 inch. The oil emulsion was added to the latex with gentle stirring. The ratio of dry rubber to oil was 67 to 33 by volume.

Carbon black dispersion was added quickly to the latex in the ratio of 47.5 parts of carbon black per hundred parts by weight of rubber plus oil. Stirring was delayed until addition was complete. Stirring was then carried out very vigorously for approximately 30 seconds to ensure rapid homogenisation of the mixture. Thickening soon set in and subsequent slow stirring caused the first formed flocs to aggregate until coagulation was completed. The serum, which was free from rubber and oil and contained only a very small amount of carbon black, was removed through a wire mesh filter.

The coagulum was converted into a fine crumb by passing through a rotary cutter and dried on trays in gently moving air at 140°F. Moisture content was reduced to 0.4% in 48 hours.

Example II

Natural rubber field latex having a dry rubber content of 34.0% was protected by the addition of 0.1% ammonia (based on weight of latex). A paraffinic mineral extending oil, sold under the Trade Mark "Vitrea" 27, was emulsified with half its weight of water by means of ammonium oleate (0.5% oleic acid dissolved in the oil and 0.1% ammonia dissolved in the water). The ratio of dry rubber to oil was 70 to 30 by volume.

Carbon black of the type known as ISAF was dispersed as in the previous Example.

Latex and oil from one container and carbon black dispersion from another were separately metered through two metering pumps of the reciprocating piston type. The two streams entered the mixer described earlier and the emerging coagulum was collected on a wire mesh filter. Carbon black was present in the ratio of 50 parts per 100 parts by weight of rubber plus oil.

The coagulum was passed through a rotary cutting machine and the resultant fine crumb dried in a layer about 5 inches deep by means of a forced draught of air through the material at 180°F. The moisture content was 0.5% after 6 hours.

It will be seen that the present invention utilises the known property of flocculating rubber latices possessed by carbon black in a controlled manner in order to bring about the production of masterbatches of natural rubber containing carbon black in a simple and convenient manner in such a way as to eliminate the disadvantages associated with the incorporation of dry carbon black into rubber in conventional mixing mills.

The present invention therefore makes it possible to produce carbon black masterbatches of natural rubber which will overcome the disadvantages to manufacturers of rubber goods of the use of carbon black itself by a simple and convenient process using field latex in a factory on the plantation.

WHAT WE CLAIM IS:—

1. A process for the manufacture of a natural rubber/carbon black masterbatch which comprises adding an aqueous dispersion of carbon black, stabilised with a dispersing agent, to a natural rubber field latex, optionally preserved by the use of up to 0.2% by weight of ammonia, agitating to effect uniform mixing of the carbon black dispersion in said latex and continuing agitation until the rubber flocculates and finally coagulates and thereafter separating the coagulum from the serum, the carbon black being used in amounts up to 100% of the weight of the rubber in the latex.

2. A process according to claim 1, wherein an aqueous emulsion of a mineral oil containing an emulsifying agent is intimately admixed with the latex prior to the admixture therewith of the carbon black.

3. A process according to claim 2, wherein the emulsifying agent is a soap.

4. A process according to claim 3, wherein the soap is a laurate or oleate of sodium, potassium or ammonia or is tetraethylene pentamine oleate.

5. A process according to any of the preceding claims, wherein the onset of thickening is delayed by the addition of a protective agent to the latex.

6. A process according to claim 5 wherein the protective agent is a surface-

especially of flex resistance and of cut-growth resistance.

We find that it is possible to use the extender oil in amounts up to 70% by weight of the rubber in the latex.

The following Examples are given to illustrate the manner in which the invention may be carried into effect and the percentage figures quoted therein are calculated by weight unless otherwise stated.

Example I

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Carbon black dispersion was added quickly to the latex in the ratio of 47.5 parts of carbon black per hundred parts by weight of rubber plus oil. Stirring was delayed until addition was complete. Stirring was then carried out very vigorously for approximately 30 seconds to ensure rapid homogenisation of the mixture. Thickening soon set in and subsequent slow stirring caused the first formed flocs to aggregate until coagulation was completed. The serum, which was free from rubber and oil and contained only a very small amount of carbon black, was removed through a wire mesh filter.

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It will be seen that the present invention utilises the known property of flocculating rubber latices possessed by carbon black in a controlled manner in order to bring about the production of masterbatches of natural rubber containing carbon black in a simple and convenient manner in such a way as to eliminate the disadvantages associated with the incorporation of dry carbon black into rubber in conventional mixing mills.

The present invention therefore makes it possible to produce carbon black masterbatches of natural rubber which will overcome the disadvantages to manufacturers of rubber goods of the use of carbon black itself by a simple and convenient process using field latex in a factory on the plantation.

WHAT WE CLAIM IS:—

1. A process for the manufacture of a natural rubber/carbon black masterbatch which comprises adding an aqueous dispersion of carbon black, stabilised with a dispersing agent, to a natural rubber field latex, optionally preserved by the use of up to 0.2% by weight of ammonia, agitating to effect uniform mixing of the carbon black dispersion in said latex and continuing agitation until the rubber flocculates and finally coagulates and thereafter separating the coagulum from the serum, the carbon black being used in amounts up to 100% of the weight of the rubber in the latex.

2. A process according to claim 1, wherein an aqueous emulsion of a mineral oil containing an emulsifying agent is intimately admixed with the latex prior to the admixture therewith of the carbon black.

3. A process according to claim 2, wherein the emulsifying agent is a soap.

4. A process according to claim 3, wherein the soap is a laurate or oleate of sodium, potassium or ammonia or is tetraethylene pentamine oleate.

5. A process according to any of the preceding claims, wherein the onset of thickening is delayed by the addition of a protective agent to the latex.

6. A process according to claim 5 wherein the protective agent is a surface-



active agent.

7. A process according to any of the preceding claims wherein two separate streams of the latex and of the carbon black dispersion are metered into a totally enclosed mixer.

8. A process according to claim 7, wherein the mixer comprises two parallel shafts carrying a series of staggered projecting pins which intermesh with a small clearance between each other and the casing of the mixer with two perforated delivery tubes so disposed within the casing that the two metered streams impinge on each other between the rotating shafts.

9. A process according to claim 8, wherein the pins are each formed with a pitched face to impel the mixture axially of the casing.

10. A process according to claim 8 or

claim 9, wherein pitched expellers are mounted on the shafts to move the mixture to an exit tube.

11. A process according to any of claims 2 to 10, wherein the extender oil is used in amounts up to 70% by weight of the rubber in the latex.

12. The process for the manufacture of a natural rubber/carbon black masterbatch substantially as described with reference to either of the Examples.

13. Natural rubber/carbon black masterbatches when prepared by the process claimed in any of the preceding claims.

STEVENS, LANGNER, PARRY &
ROLLINSON,

Chartered Patent Agents,
Agents for the Applicants.

B.K.

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