

PATENT SPECIFICATION (11)

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(54) MASTERBATCHED SOLID RUBBER BLENDS AND METHODS OF MAKING SAME

(71) We, ASHLAND OIL INC., a corporation organized and existing under the laws of the State of Kentucky, United States of America, of P.O. Box 391, Ashland, Kentucky 41101, United States of America, 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:—

This invention relates to natural rubber blends and methods for making them. More particularly, this invention relates to techniques for extending masterbatched natural rubber produced from latex, by blending solid rubber therewith, and blends made therefrom.

Natural rubber is harvested principally as a latex. This latex, used as such, makes the highest quality rubber products. Examples of such products include technically specified rubbers, black masterbatch, pale crepe, smoked sheet and the like.

Latex is not the only source of usable rubber however. By the nature of the latex harvesting technique, for example, an appreciable amount of moist (15 to 20% or more water) solid rubber is formed and harvested. Much of this solid rubber is of high quality but cannot be processed in the same manner as latex, and thus cannot be formed or processed contiguously therewith. Other examples of usable solid rubber include dirty or biodegraded solid rubber obtained during harvesting and solid rubber scrap.

Ideally, and in order to obtain the highest quality rubber, all rubber should be produced from natural rubber latex. Such however would waste the high quality solid rubber obtained during harvesting (e.g. cup lump, tree lace, naturally coagulated rubber and the like) and constitute a waste of what otherwise might be a valuable and useful source of rubber—dirty or biodegraded rubber and rubber scrap.

As a possible solution to this problem, one might attempt to form a rubber from latex and blend it with one of the other rubbers to obtain a desired product. While this is possible, for many uses it is either

undesirable or unworkable. Firstly, the quality of such a blend would be degraded to the extent of the amount of solid second rubber employed. Secondly, it has been found that natural rubber tends to break down and become increasingly softer with milling. Thus the milling used to blend added to the milling necessitated in later processing would be at best detrimental.

It is known that rubber products may be upgraded by masterbatching them with carbon black. Thus a second possible solution to the above problem of making use of solid rubber might be to form the above-described blend, but in masterbatched form. If such could be properly accomplished, the carbon black would serve to offset the lower quality of the solid rubber blended with the latex rubber or in other ways increase the quality of the ultimate blend to a least an acceptable level. Without, however, the teachings of this invention, such a solution is generally unworkable. Dry blending of the rubbers with carbon black, for example, results in poor carbon-black dispersion and/or undue milling time which tends to soften the rubber. It also requires that the rubbers be processed to dryness before blending. Carbon black, on the other hand, does not mix well with wet rubber (such as cup lump or wet solid coagulum). Thus wet blending the ingredients would not appear feasible.

As further evidence of the seeming unworkable nature of employing the technique of masterbatching to the problem of using solid rubber to extend latex rubber is the fact that preloading of the latex with carbon-black and thereafter blending the preloaded latex coagulum with the solid rubber ingredient also proves unsuccessful unless the teachings of this invention are followed. It was not until recently, for example, that a satisfactory carbon-black natural latex rubber masterbatch crumb (the best form for blending) could be produced by coagulation methods. Even assuming however, the availability of this new technique (described more fully hereinafter) or, on the other hand, regardless of the coagulating-masterbatching technique employed, 100

it was found that blending is still a problem. After the masterbatched natural rubber latex coagulum is dried and blended, the blending softens the rubber too much. In addition the heavy loading with carbon black of the natural rubber latex necessary to provide the requisite amount of carbon black in the ultimate blend, tends to render the final product hard and horny. Dispersion is also quite poor, the carbon black being found to exist as discrete hard particles and lumps in the milled matrix.

From the above it is evident that there exists a definite need in the art for a technique capable of forming high quality rubber while at the same time employing solid rubber as well as latex coagulum, and the invention has been made with this in mind.

According to the invention there is provided a substantially uniform, nonhorny, extended natural rubber latex blend comprising a natural rubber and a solid rubber (as defined herein) blended therewith, the blend having dispersed therein 40 to 125 parts by weight of particulate carbon black per 100 parts by weight latex rubber and exhibiting a carbon-black dispersion of greater than 90% as measured by ASTM D-2653-67T.

The invention provides a unique, high quality rubber blend comprised of natural latex rubber, "solid" rubber and a particulate carbon black.

The initial step in the process of the invention involves forming a natural rubber masterbatch highly loaded with particulate carbon black by coagulating a latex of rubber and particulate carbon-black. The coagulum is then dried to a moisture content (e.g. usually above about 10% by weight as hereinafter more fully described) above that at which a hard and horny product, (e.g. rough, non-smooth, or with appreciable graininess or lumpiness) will be formed, and the loaded coagulum is blended with solid rubber to form thereby a rubber product blend exhibiting good dispersion qualities and other properties necessary to the easy working of the material in subsequent processing steps.

It is believed that through the provision of a finite prescribed moisture content in the masterbatched latex rubber used for blending, a successful blend, for the first time, is unexpectedly achieved.

The term "solid rubber" when used herein to describe the rubber ingredient blended with the masterbatched rubber means any solid rubber, pigmented or unpigmented other than the latex rubber of the masterbatch. Examples of such solid rubber as set forth above, include solid high quality rubber obtained during harvesting (e.g. cup lump, tree lace and naturally coagulated rubber), dirty fresh solid rubber, biodegraded solid rubber, and rubber scrap.

The term "highly loaded" is used herein in accordance with its conventional meaning in the art. Generally speaking it means using up to as much as about 125 pbw (parts by weight) of carbon black per 100 pbw of latex rubber so as to insure the requisite amount of carbon black in the ultimate blend. The lower limit will, of course, depend upon the ultimate quality of the product desired. Usually, however, a product may still be considered highly loaded at about 40 pbw of carbon black per 100 pbw latex rubber. Because of the techniques of this invention, it is found that good dispersion and substantially no horniness or hardness occurs in the coagulum and/or final blend despite the employment of such a large amount of carbon black.

The masterbatch for use of this invention may be formed by any known and/or conventional technique for masterbatching a natural rubber from its latex with carbon-black. One relatively simple technique which may be employed for the purposes of this invention is to add to the natural rubber latex the requisite amount of particulate carbon black in aqueous slurry form and the requisite amount of coagulation acid, with agitation sufficient to insure dispersion of the particles of carbon black in the rubber. The coagulum so formed is then collected and dried to the requisite moisture content by any conventional technique such as screening, centrifuging or the like.

Another, and particularly preferred technique which may be employed to form the masterbatches used in this invention, is that as disclosed in our copending Application No. 14993/73 (Serial No. 1,421,012).

Generally speaking, this copending application discloses a unique process for providing a high quality natural rubber black masterbatch crumb which includes admixing the natural rubber latex and an aqueous slurry of carbon black with an acid, and subjecting the resulting coagulum to concurrent agitation and comminution sufficient to form a crumb of commercially acceptable qualities. Prior to or during coagulation the natural rubber latex is destabilized by heating it to a temperature of about 50°C. A coagulation aid which is a cationic material capable of destabilizing the latex is added prior to or simultaneously with the admixing of the latex with the slurry so as to destabilize further the latex.

For the purposes of the present invention we have found that the addition of the cationic coagulation aid is not essential except in the case in which the natural rubber latex is a fresh field latex.

In the present invention, the crumb, once formed, is collected and dried to the requisite moisture content as described. The wet crumb so formed is found uniquely applic-

able for blending with solid rubber in accordance with the teachings of this invention.

The upper limit of the moisture content is usually one dictated by convenience and economy. Theoretically a moisture content of 100% by weight or more could be used. However, because of the simplicity of known mechanical drying techniques, it is usually preferred to keep the moisture content below about 50% by weight. On the other hand, and as discussed above, the lower limit of the moisture content is important to obtaining the desired results of this invention. Generally speaking the moisture content should be above that which will result in a hard and horny product and prevent good dispersion of the carbon-black in the ultimate blend. For most coagulums and particularly those produced from the two above-described techniques, this means a moisture content greater than about 10% by weight and preferably greater than about 15% by weight. For the purposes of this invention, moisture contents of about 18—35% by weight are usually optimum, particularly when the coagulum is that formed by the technique of the aforementioned copending application.

While the overall moisture content is important, for best results, local dry spots should also be avoided. Such local dry spots are best avoided by using only conventional mechanical drying techniques to effect drying and avoiding the use of thermal drying techniques which could cause uneven drying and thus contaminating local dry spots.

Examples of conventional mechanical drying equipment useful in accordance with this invention are basket centrifuges, vacuum screens plus pressure and internal screw type dewatering equipment. A particularly preferred mechanical drying apparatus useful in carrying out this invention is a French Rubber Dewatering Screw Press manufactured by French Oil Mill Machinery, Piquette, Ohio.

It is important to load the masterbatch with sufficient carbon black to insure the optimum amount in the final blend. This usually means that more carbon black will be employed than would normally be employed when forming a product from the rubber latex alone and thus the use of the term "highly loaded" as set forth above. While the actual amount of carbon black will vary as the ratio of solid rubber and masterbatch varies and also as the desired ratio of carbon black and rubber in the final product varies, generally speaking, the carbon black is employed as described above, in an amount of about 40 to 125 parts by weight carbon black to 100 latex rubber.

The carbon black is preferably formed into an aqueous slurry prior to admixing it

with the latex. This insures good distribution during coagulation. While any ratio of carbon-black to water may be employed to form the slurry, it is preferred that the slurry contain about 5 to 7% by weight of carbon-black.

A particularly preferred particulate carbon-black for the purposes of this invention is one having a particle size such that greater than 99% thereof will pass through a 325 mesh screen (U.S. sieve size). Such a carbon black is sold as ISAF-LS carbon black under the trade designation N-219 by Ashland Chemical Co. Other useful carbon-blacks which are commercially available include FEF, SAF, HAF, and the like.

The acid employed to effect coagulation may be any of the acids well known to the art and useful for this purpose. Examples of such acids include acetic, formic, sulphuric, phosphoric, and the like, and mixtures of these acids. The acid is usually employed in amounts sufficient to adjust the pH of the medium to about 4.0 to 6.5 and thus to cause coagulation. A particularly preferred acid is formic acid.

In addition to the latex pigment, and acid, other conventional additives may be employed for their known effects. For example, extender oils (to soften the coagulum) and/or antioxidants (to prevent oxidation of the latex) may be added to the coagulation medium or to the starting materials.

Examples of such extender oils include both aromatic and naphthenic extender oils as well as the more highly aromatic oils. They are preferably employed as a water emulsion having a total oil content of up to about 50%.

Examples of antioxidant materials suitable for use in this invention include such conventional antioxidants as a nonylated diphenylamine antioxidant sold by the Uniroyal Chemical Division under the trademark Polylyte, N-alkyl-N-phenyl-p-phenylene diamine sold by the Uniroyal Chemical Division under the trademark Flexzone 7L, an alkylated Bisphenol sold by the Uniroyal Chemical Division under the trademark Naugawhite, a reaction product of diphenylamine and acetone sold by the Uniroyal Chemical Division under the trademark BLE, and an alkylated phenol sold by Harwick Standard Chemical Company under the trademark Nonox WSL.

Where antioxidant is added into the process, it is also preferably added in the form of a water emulsion with an antioxidant concentration of up to about 20%. The antioxidant is added, when used, in an amount of from about 0.5 to about 1.25 parts based on the weight of the rubber in the final product. The addition of antioxidant in excess of 1.25 is possible but in many cases makes little or no further im-

provement in the properties of the resulting product.

The coagulation aid employed when using the aforesaid technique of the copending application to form the masterbatch may be any cationic material capable of destabilizing the latex. Such materials as those currently employed in the art to "clarify" a latex liquor may be used. Particularly preferred are the cationic polyamines and especially those of a high molecular weight (i.e. 1,000,000 to 10,000,000). One specific example of such a polyamine is the polymer formed from the condensation polymerization of a diamine and a dialkyl halide. Generally speaking these coagulation aids are found necessary when coagulating fresh field latex and are often found desirable when employing the other natural rubber latices. The amount employed will vary with the type latex chosen, but generally about 0.2—2.0 parts by weight (based upon the contained polymer content) is sufficient to achieve the degree of destabilization required.

Any natural rubber latex may be employed for the purposes of this invention examples of which include: fresh field latex, evaporation concentrated natural latex and centrifugally concentrated natural latex as well as mixtures of these. Fresh field latex is particularly preferred for the purposes of this invention because of the economics involved in such a system and the quality of product obtained.

Other polymeric materials, in addition to the solid rubber may be blended with the masterbatched natural latex rubber. For example, various synthetic rubbers, such as those produced by the techniques of United States Patent Specification No. 3,108,983 may be employed to impart certain desired properties to the ultimate product. Such rubbers would include SBR, polybutadiene, polyisoprene, and the like.

The blending of the masterbatch with the solid rubber is accomplished preferably by internal mixers such as by a Banbury mixer, or screw type extruder such as a French Mill. The blending should be carried out for a time in the range from 1 to 20 minutes since further blending may render the rubber unduly soft. For this invention, excellent dispersion without undue softening is usually obtainable within 1 to 20 minutes using conventional blending equipment.

The amount of masterbatch natural rubber employed will, of course, depend upon the quality of the ultimate product desired. Thus as little as about 1% or less of the ultimate blend may be masterbatch rubber or as much as 95% or more may be masterbatch rubber. For most purposes it has been found adequate to blend the masterbatch rubber with the solid extender rubber in the ratio by

weight respectively of about 1:5 to about 5:1. In those instances where the solid rubber is hard (e.g. pigmented or unpigmented scrap rubber) or in smoked sheet form, it is preferred to premasticate it prior to blending so as to insure good dispersion and blending generally.

In a particularly preferred mode of carrying out the subject invention, the following process steps are conducted:

(a) admix natural latex with the requisite amount of carbon black wherein the weight ratio (of the solids) is about 1:1;

(b) shortly thereafter or simultaneously therewith add the coagulation aid together with coagulation aid (if any), heat, etc., in an amount to cause the pH of the coagulating medium to drop to about 4.0 to 6.5;

(c) stir while coagulating to assure dispersion of carbon black in masterbatch; (in a particularly preferred technique the stirring not only agitates but comminutes in accordance with the teachings of the aforesaid copending application);

(d) collect the coagulum as by screening and dewater to a moisture content of 10 to 40% by weight using a basket centrifuge or other mechanical device;

(e) blend the coagulum with a natural rubber such as semi-dried cup lump or a dry rubber of any kind for about 1 to 10 minutes in a Banbury mill; (the moisture content of the solid rubber is not critical and may be adjusted for convenience or left as it is);

(f) dry the blend at a mild temperature (e.g. 60 to 70°C.).

Thereafter, and optionally, the blend so formed may be formed into a commercial product such as, for example, a sheet by:

(g) compounding the dry stock in a Brabender Plasticorder or a Banbury mixer either alone or with pigments (other than carbon black), etc., and

(h) sheeting the product of (g) on a roll mill.

When so produced, the products of this invention exhibit carbon black dispersions of greater than 90% and usually greater than 95% (as measured by ASTM D-2663-67T). In addition they are rubbers exhibiting physical properties equal to a high quality masterbatch made entirely from latex.

This invention will now be illustrated with reference to the following Examples in which all parts and percentages are by weight unless otherwise stated. Examples 3 and 7 to 11 are provided for comparison.

EXAMPLE 1

Fresh field natural latex suitably stabilized, i.e. with ammonia, is diluted with water to a total solids content of 18.9%.

- 5 ISAF-LS carbon black, sold under the trade designation N-219 by Ashland Chemical Co. is placed in a tank with sufficient water to equal approximately 6.0% solids. The carbon black is reduced to a
10 finely divided state in the water by recirculating through suitable piping with a centrifugal pump or by other suitable means until less than 1% of the black is retained on a 325 mesh screen. Total solids content is
15 found to be 5.2%.

A highly aromatic oil suitable for rubber processing is emulsified by suitable means using a fatty acid such as oleic acid and a caustic as emulsifying agent. Total solids content is found to be 48.7%.

Polylite, an antioxidant, is emulsified by suitable means using a fatty acid such as oleic acid and a caustic as emulsifying agent. Total oil concentration of the emulsion is found to be 20.4%.

A typical recipe for a masterbatch using the above materials together with the equivalent fluids is as follows, the numerical amounts indicating parts by weight:

		Solids Proportion (parts by weight)	TSC or Concentration of Fluid	Equivalent Fluid
35	Latex	100	18.9	529
	Carbon Black			
	Slurry	100	5.2	1921
	Oil Emulsion	20	48.7	41
	Antioxidant			
40	Emulsion	2.5	20.4	12.4

The various fluids are now supplied by Foxboro Magnetic Flow Meters and proportioning pumps, and in the proportions indicated by the recipe to a high shear coagulator such as an Ashland coagulator all of which are described in the aforesaid copending application.

- 45 The volume of the coagulator is 4 gallons with a throughput of 6.5 gal/min and a residence time of about $\frac{1}{2}$ minute. The coagulator is operated at 1400 RPM with a 3 H.P. motor. Steam is introduced into the coagulator to raise the fluid temperature to about 60 to 65° C. A dilute solution of formic acid plus Nalco 107 as a coagulation aid is added at such a rate as to reduce the effluent pH to between 5.0 and 5.5.

- 55 Nalco 107 polyamine is added at the rate of 5 to 10 parts per 100 parts of the acid. It is mixed with the acid solution as a matter of convenience.

- 60 The effluent from the coagulator is found to consist of a masterbatch crumb of between $\frac{1}{8}$ to $\frac{3}{8}$ inches with essentially no excessively fine material (i.e. less than 1% passing through a 100 mesh screen (U.S. sieve size) and a water clear serum.

- 65 The coagulated crumb is then collected and dewatered in a basket centrifuge to a moisture content of 31%. Cup lump rubber having a moisture content of 17% is now placed in a Banbury internal mixer with the masterbatch in an amount of 323 parts by weight cup lump to 120.5 parts by weight crump, and the two rubbers are mixed approximately five minutes. The mixed masterbatch is then removed from the Banbury and dried at about 70° C. The blend is

found to be uniformly mixed and ASTM-D-2663-67T test indicates 95% or more dispersion of carbon black.

EXAMPLE 2

Example 1 is repeated except that a pre-masticated dried smoked sheet of solid rubber is used in place of the cup lump. The batch is again found to be well mixed and with good carbon black dispersion.

EXAMPLE 3

Example 1 is repeated except that the masterbatch crumb is dried to less than 1% moisture content before it is mixed with the cup lump. The end product is found to be very poorly mixed with appreciable graininess and lumpiness and entirely unsatisfactory for commercial use.

EXAMPLE 4

Example 1 is repeated except that a large particle size black (such as FEF) is used in place of the small particle ISAF Black. The final product is again found to be well mixed and to have good carbon black dispersion.

EXAMPLE 5

The ingredients for making a masterbatch as set forth in Example 1 are simply admixed together with stirring in heir indicated amounts. To this stirred mixture, is then added, a sufficient amount of coagulating acid to cause coagulation of the rubber latex therewithin. Agitation is sufficient such that comminution is held at a minimum but the carbon black still is adequately dispersed throughout the mixture. A suitable anti-

oxidant (Polylite) is added to the mixture such that the final product (parts by weight) contains the following:

Natural Rubber — 100
ISAF-LS Carbon Black — 100
Anti-Oxidant — 1.25

The final product (masterbatch) is then dried to less than 1% moisture content at a mild temperature (60 to 70° C.). 800 grams of the product are charged together with 400 grams of a premasticated natural solid rubber (Dynat) in a #B-R Banbury mixer and milled for four minutes and collected. The batch is then sheeted on a roll mill. The sheet is extremely rough and knobby (horny).

The product is again placed on a roll mill and milled for another ten minutes. There is essentially no change in the appearance of this sheeted product.

EXAMPLE 6

The freshly coagulated masterbatch as described in Example 5 is not dried as described therein, but rather is dewatered using a basket centrifuge to a moisture content of about 40%. 1200 grams of this masterbatch together with 360 grams of the Dynat natural solid rubber (premasterbatch) are blended in a Banbury mixer for two minutes and then charged into a #B-R Banbury mixer as in Example 5, and milled for four minutes and collected. The product is then dried at a mild temperature (about 70° C.). The dried product is compounded in a Brabender Plasticorder in an 8 minute cycle and sheeted off on a roll mill. The sheet is smooth and uniform. A test for carbon black dispersion carried out according to ASTM procedure D-2663-67T indicates a 98.94% dispersion.

EXAMPLE 7

800 grams of Heveacrum C-V-5 (a top grade solid dry natural rubber produced from latex) is charged into a Banbury mixer with 400 grams of ISAF-LS carbon black and mixed in a 4 minute cycle. A portion of this product is then compounded in a Brabender Plasticorder in an 8 minute cycle and sheeted off onto a roll mill. The sheet is smooth and uniform. A test for carbon black dispersion carried out according to ASTM procedure D-2663-67T indicates only an 84.88% dispersion of the carbon black. This example serves to show that the subject invention achieves better carbon black dispersion than a high quality dry latex rubber blended with carbon black, despite the fact that the subject invention is also blending a solid rubber with the latex rubber.

EXAMPLE 8

Four coagulations were made with a fresh field natural rubber latex using 100 parts

carbon black per 100 parts latex rubber by the simple technique employed as described generally in Example 5 except that the more rapid agitation normally used for natural rubber masterbatching was used. Two of these coagulations were made with an emulsifier oil (HI-AR) in an attempt to soften the ultimate blend. When the technique was employed using agitation normally employed for natural rubber masterbatching, the crumb was quite soft and tended to break down excessively.

EXAMPLES 9 to 12

In contrast to Example 8, 4 smaller batches made in relatively small containers and employing only a small hand paddle for agitation, proved to form a crumb which was filterable and readily drier. These four crumbs from the smaller batches were then processed as follows: The first coagulation crumb, Example 9 (without emulsifier oil), was dried to about 1% moisture content and blended in a 2:1 weight ratio with premasticated rubber that had been coagulated from centrifuged latex. The blend formed by milling in a Banbury mixer for four minutes and then blended further on a standard mill for approximately 10 minutes. A non-uniform blend was obtained, in that most of the masterbatch never blended with the solid centrifuged latex rubber. The final slab produced was very rough with large chunks of masterbatch therein.

The next two coagulated crumbs (Examples 10 and 11) were formed in the same way as the first crumb, except that they had added thereto 10 and 20 parts of emulsifier oil respectively, which amounted to 5 and 10 parts oil respectively based upon the final blend. These samples were dried to a moisture content of less than about 1% and blended with premasticated Dynat. These two milled blends were somewhat better than the first blend but they were far from satisfactory having low dispersion and excessive lumpiness.

The fourth coagulation, Example 12 (without emulsifier oil) was produced in the same manner as the first, except that the masterbatch was not dried prior to blending. Rather, it was allowed to remain wet (i.e. greater than 10% moisture content). The blend so produced was a reasonably uniform blend, which, under the microscope did reveal some particles of undispersed masterbatch, but such non-dispersion was sufficiently minimal such that the blend could be termed "reasonably uniform" and quite acceptable for many purposes.

The words "Foxboro" and "Dynat" are registered Trade Marks.

WHAT WE CLAIM IS:—

1. A substantially uniform, nonhorny, 130

oxidant (Polylite) is added to the mixture such that the final product (parts by weight) contains the following:

- 5 Natural Rubber — 100
- ISAF-LS Carbon Black — 100
- Anti-Oxidant — 1.25

10 The final product (masterbatch) is then dried to less than 1% moisture content at a mild temperature (60 to 70° C.). 800 grams of the product are charged together with 400 grams of a premasticated natural solid rubber (Dynat) in a #B-R Banbury mixer and milled for four minutes and collected. The batch is then sheeted on a roll mill. The sheet is extremely rough and knobby (horny).

15 The product is again placed on a roll mill and milled for another ten minutes. There is essentially no change in the appearance of this sheeted product.

EXAMPLE 6

25 The freshly coagulated masterbatch as described in Example 5 is not dried as described therein, but rather is dewatered using a basket centrifuge to a moisture content of about 40%. 1200 grams of this masterbatch together with 360 grams of the Dynat natural solid rubber (premasterbatch) are blended in a Banbury mixer for two minutes and then charged into a #B-R Banbury mixer as in Example 5, and milled for four minutes and collected. The product is then dried at a mild temperature (about 70° C.).

30 The dried product is compounded in a Brabender Plasticorder in an 8 minute cycle and sheeted off on a roll mill. The sheet is smooth and uniform. A test for carbon black dispersion carried out according to

35 ASTM procedure D-2663-67T indicates a 98.94% dispersion.

EXAMPLE 7

45 800 grams of Heveacrumb C-V-5 (a top grade solid dry natural rubber produced from latex) is charged into a Banbury mixer with 400 grams of ISAF-LS carbon black and mixed in a 4 minute cycle. A portion of this product is then compounded in a

50 Brabender Plasticorder in an 8 minute cycle and sheeted off onto a roll mill. The sheet is smooth and uniform. A test for carbon black dispersion carried out according to

55 ASTM procedure D-2663-67T indicates only an 84.88% dispersion of the carbon black. This example serves to show that the subject invention achieves better carbon black dispersion than a high quality dry latex rubber blended with carbon black, despite the fact that the subject invention is

60 also blending a solid rubber with the latex rubber.

EXAMPLE 8

65 Four coagulations were made with a fresh field natural rubber latex using 100 parts

carbon black per 100 parts latex rubber by the simple technique employed as described generally in Example 5 except that the more rapid agitation normally used for natural rubber masterbatching was used. Two of these coagulations were made with an emulsifier oil (HI-AR) in an attempt to soften the ultimate blend. When the technique was employed using agitation normally employed for natural rubber masterbatching, the crumb was quite soft and tended to break down excessively.

EXAMPLES 9 to 12

80 In contrast to Example 8, 4 smaller batches made in relatively small containers and employing only a small hand paddle for agitation, proved to form a crumb which was filterable and readily drier. These four crumbs from the smaller batches were then processed as follows: The first coagulation crumb, Example 9 (without emulsifier oil), was dried to about 1% moisture content and blended in a 2:1 weight ratio with pre-

85 masterbatched rubber that had been coagulated from centrifuged latex. The blend formed by milling in a Banbury mixer for four minutes and then blended further on a standard mill for approximately 10 minutes. A non-uniform blend was obtained, in that

90 most of the masterbatch never blended with the solid centrifuged latex rubber. The final slab produced was very rough with large chunks of masterbatch therein.

95 The next two coagulated crumbs (Examples 10 and 11) were formed in the same way as the first crumb, except that they had added thereto 10 and 20 parts of emulsifier oil respectively, which amounted to 5 and 10 parts oil respectively based upon the final blend. These samples were dried to a moisture content of less than about 1% and blended with premasterbatched Dynat. These

100 two milled blends were somewhat better than the first blend but they were far from satisfactory having low dispersion and excessive lumpiness.

105 The fourth coagulation, Example 12 (without emulsifier oil) was produced in the same manner as the first, except that the masterbatch was not dried prior to blending. Rather, it was allowed to remain wet (i.e. greater than 10% moisture content). The blend so produced was a reasonably uniform blend, which, under the microscope did reveal some particles of undispersed master-

110 batch, but such non-dispersion was sufficiently minimal such that the blend could be termed "reasonably uniform" and quite acceptable for many purposes.

115 The words "Foxboro" and "Dynat" are registered Trade Marks.

WHAT WE CLAIM IS:—

1. A substantially uniform, nonhorny, 120

- extended natural rubber latex blend comprising a natural latex rubber and a solid rubber (as defined herein) blended therewith, the blend having dispersed therein 40 to 125 parts by weight of particulate carbon black per 100 parts by weight of latex rubber and exhibiting a carbon black dispersion of greater than 90% as measured by ASTM D-2653-67T.
2. A blend as claimed in Claim 1 in which the carbon black dispersion is greater than about 95%.
3. A blend as claimed in Claim 1 or Claim 2 in which the natural latex rubber and solid rubber (as defined herein) are employed in a weight ratio of 1:5 to 5:1 respectively.
4. A blend as claimed in any preceding claim in which the solid rubber (as defined herein) is cup lump, tree lace, naturally coagulated rubber, dirty fresh solid rubber, biodegraded solid rubber, rubber scrap or mixtures thereof.
5. A blend substantially as herein described with reference to any of Examples 1, 2, 4, 6 and 12.
6. A process for forming a substantially uniform, nonhorny, extended natural latex blend, comprising forming a natural rubber masterbatch by coagulating a latex of rubber and 40 to 125 parts by weight of particulate carbon black per 100 parts by weight of latex rubber, drying the coagulum formed to a moisture content above that at which a hard and horny product will be formed, and blending the coagulum with a solid rubber (as defined herein) for a time sufficient to achieve a carbon black dispersion of greater than 90% as measured by ASTM D-2653-67T in the range 1 to 20 minutes.
7. A process as claimed in Claim 6 in which the solid rubber (as defined herein) is cup lump, tree lace, naturally coagulated rubber, dirty fresh solid rubber, biodegraded solid rubber, rubber scrap or mixtures thereof.
8. A process as claimed in Claim 6 or Claim 7 in which the coagulum is dried to a moisture content above 10% by weight.
9. A process as claimed in Claim 6 or Claim 7 in which the coagulum is dried to a moisture content of 18 to 35% by weight.
10. A process as claimed in Claim 8 or Claim 9 in which the drying is done mechanically and without the addition of heat.
11. A process as claimed in any of claims 6 to 10 in which the coagulum is a crumb and the coagulation of the latex of rubber and particulate black comprises admixing the natural rubber latex with an aqueous slurry of carbon black and a coagulation acid, subjecting the resulting coagulum to concurrent agitation and comminution sufficient to form a crumb and prior to or during the admixing of the latex with the slurry and the agitation and comminution, destabilizing the natural rubber latex by heating it to a temperature of above 50° C.
12. A process as claimed in any of claims 6 to 11 in which the natural rubber latex is a fresh field latex and a coagulation aid is added prior to or simultaneously with the admixing of the latex with the slurry and the agitation and comminution.
13. A process as claimed in any of claims 6 to 12 in which the blend also includes an extender oil, an antioxidant, or a synthetic polymeric material or mixtures thereof.
14. A process as claimed in any of claims 6 to 13 in which the blend exhibits a carbon black dispersion of greater than about 95% as measured by ASTM D-2663 67T.
15. A process for forming a substantially uniform nonhorny, extended natural rubber latex blend substantially as herein described with reference to any of Examples 1, 2, 4, 6 and 12.
16. A substantially uniform, non horny, extended natural rubber latex blend, when prepared by the process according to any of claims 6 to 15.

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