

1,082,844



# PATENT SPECIFICATION

1,082,844

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## COMPLETE SPECIFICATION

### NO DRAWINGS

### Reinforced Latex

We, THE GOODYEAR TIRE & RUBBER COMPANY, a corporation organized under the laws of the State of Ohio, United States of America, of 1144 East Market Street, Akron, Ohio, 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 reinforced high molecular weight rubber, particularly reinforced rubber latex, to a method of compounding a rubber latex with a reinforcing agent and to uses for the reinforced latex and rubber resulting therefrom.

The true reinforcement of rubber in the latex form has been a problem of the latex chemist ever since rubber latex has been known and used commercially. Many investigators have reported various means for solving this problem, but in most instances true reinforcement is not obtained, particularly when working with such reinforcing agents as carbon black.

The present invention is concerned with a method of reinforcing a rubber in its latex form which comprises preblending a reinforcing agent with a water soluble phenolic resin carrier which is compatible with both the rubber latex and with the reinforcing agent and then blending the preblend of carrier and reinforcing agent with the rubber latex in order to intimately associate both the carrier and the reinforcing agent with the particles of the rubber in the latex to thereby produce a reinforced rubber latex. The rubber latex may also be compounded with other ingredients including accelerators, activators, curing agents, emulsifiers, and, if need be, thickeners. The compounding ingredients may be added directly to the rubber latex, preferably before, but also may

be added during or after the reinforcing agent is incorporated into the rubber latex with the aid of the carrier. The reinforced rubber resulting from the drying of a film of the reinforced rubber latex or from the coagulation of the reinforced rubber latex possesses an improved tensile strength far superior to the same rubber made from the same latex containing the same reinforcing agent but added in a manner other than the manner disclosed by the present invention.

More particularly, the present invention concerns the reinforcement of a synthetic rubber in latex form, for example, a butadiene/25 styrene rubber latex with a reinforcing filler, such as any of the well-known reinforcing carbon blacks, particularly by first adding the reinforcing filler to the carrier and then adding this blend of components to the rubber latex.

The carrier is a water soluble phenolic resin compatible both with the reinforcing agent and with the rubber component of the latex. This function of compatibility of the carrier with both the rubber of the latex and the reinforcing agent permits a true association in a reinforcing manner of the reinforcing agent with the rubber latex. Carbon blacks are well-known reinforcing agents, but have a tendency to be repelled by the rubber particles when in a latex and therefore true reinforcement of the rubber particles is not achieved.

The water-soluble phenolic resins used as carriers in the present invention, particularly the condensates resulting from the reaction of an aldehyde with a phenol, are successful in bringing out the intimate association of the reinforcing agent with the rubber particles of the latex. Particularly valuable as a carrier in the present invention are the condensates resulting from the reaction of

formaldehyde and a polyhydric phenol such as resorcinol.

It is theorized that the carrier is absorbed on the surface of the reinforcing agent used, for example, carbon black, thus becoming intimately associated with the reinforcing agent in a manner somewhat akin to the functioning of an emulsifier where one portion of the molecule is soluble in oil and the other portion is soluble in water. In the present case, the carrier is also soluble in water and fully compatible with the rubber portion of the latex and therefore being intimately associated with the reinforcing agent and being soluble in or compatible with the rubber particles of the latex, carries the reinforcing agent into intimate contact with the rubber particles, thus producing a true reinforcement of the rubber particles.

The present method of reinforcing rubber latex using a compatibilizing carrier of the nature described permits for the first time the true reinforcement of rubber in latex form without the necessity of breaking down the molecular weight of the rubber on a mill in order to permit the milling of the reinforcing agent into the rubber.

The present invention thus preserves the molecular weight of the rubber being treated since the reinforcement thereof is being done in the latex form and makes possible for the first time the vulcanization of the reinforced rubber at a molecular weight level of the rubber higher than has heretofore been possible when working in the dry state. Thus, dry rubber broken down on the mill from, for example, a molecular weight of from about 400,000 to about 250,000 (as determined by inherent viscosity measurements) is then cured. The 250,000 molecular weight rubber will have properties inferior to a 400,000 molecular weight rubber cured in the same manner. In the present invention the rubber recovered from the reinforced rubber latex would have, for example, an undisturbed molecular weight of 400,000, which then may be cured to produce a rubber having properties superior in regard to tensile strength, elongation, etc., to the properties of the same rubber if the rubber were broken down on a mill during mixing with carbon black and then cured.

As a result of the present invention, improved dipped goods may be manufactured using the reinforced rubber latex. For example, gloves having improved properties may be made by dipping a form in the reinforced rubber latex and, equally important, a fabric may be coated with the reinforced rubber latex which has been thickened to the desired viscosity and then dried to form a layer of rubber on the surface of the fabric without producing a grain effect as otherwise produced when dry rubber is calendered onto the fabric. Another important use for

the reinforced latex is in, for example, building up a tyre tread on a pneumatic tyre carcass of fabric plies by rotating the fabric carcass in the reinforced rubber latex which has been thickened to the desired degree and then drying each layer of latex as it is deposited thereon until the desired thickness of tread is produced. The green tyre is then placed in a mold and cured to produce a tyre having improved properties.

Any rubber in latex form may be reinforced in accordance with the process of this invention, including natural rubber and any of the known synthetic rubbers, particularly the diene rubbers and especially the conjugated diene hydrocarbon rubbers that are well-known in the synthetic rubber art and as described in greater detail in US 2,935,485, as well as the vinylpyridine/diene rubber copolymers made, for example, in the manner described in US 2,634,250.

Any reinforcing agent which may be colloidally dispersed in a composition compatible and/or dispersible in rubber or dispersible substantially to that degree obtained in a colloidal dispersion may be used, particularly the well-known reinforcing carbon blacks that are used in the rubber industry for the purpose of reinforcing or improving the tensile strength of rubber.

The following examples illustrate how the invention may be practiced. All parts are by weight unless otherwise identified.

#### EXAMPLE 1

Resin/Carbon Black/Rubber Latex Mixture 100

Three parts of water solution containing 75% solids of a resorcinol/formaldehyde resin and hereinafter referred to as R/F resin and prepared generally in the manner disclosed below is dissolved in 30 parts of a 0.5% sodium hydroxide solution. To this carrier solution is added 30 parts of carbon black with thorough stirring to form a preblend of a carbon/resin mixture. This mixture is allowed to age. To this aged mixture is then added 250 parts of a 40% solids rubber latex, in this instance a latex of a 75 butadiene/25 styrene copolymer, and aged for 4 hours. The resulting carbon black reinforced rubber latex has a pH of about 10. The resorcinol/formaldehyde resin is made by reacting one mol of resorcinol with 0.7 mol of formaldehyde in the presence of 0.1 part of sodium hydroxide at 70°F. until the reaction is complete.

#### EXAMPLE 2

Cured film of carbon black reinforced latex

The carbon black reinforced rubber latex of Example 1 was compounded with 2 parts of sulfur, 5 parts of zinc oxide, 3 parts of stearic acid, 0.2 part of disphenyl guanidine, and 0.7 part of benzothiazyl disulfide.

A film of rubber from this compounded carbon black reinforced rubber latex was cast on a glass plate and dried for 1 hour

and then cured under a pressure of 10 psi at 290°F. for various lengths of time as indicated in the table below and found to have developed the tensile strengths as indicated in contrast to the tensile strengths developed by the identical compounding of the same rubber latex used in Example 1 above without reinforcement thereof with carbon black in the manner described in Example 1.

**TABLE I**  
*Carbon Black Reinforced Latex Film Control*

|               |                 |         |
|---------------|-----------------|---------|
| 10 minutes    | Tensile 360 psi | — psi   |
| 15 20 minutes | „ 1250 psi      | — psi   |
| 30 minutes    | „ 2320 psi      | 350 psi |
| 40 minutes    | „ 2140 psi      | 450 psi |

The reinforced rubber latex of this invention, when compounded with conventional accelerators, activators and curing agents, may be cured at lower temperatures and for less time to produce acceptable properties of tensile, elongation, hardness, etc., than when the latex is compounded with a reinforcing agent in a manner other than the manner disclosed in this invention. For example, the latex of Example 1, when dried into a rubber film and cured at 300°F. for 10 minutes produces a tensile strength of 2800 psi at 400% ultimate elongation having a Shore D hardness of 6C. Without the use of the present invention tensile strengths of only 600 psi are developed only after heating from 350-400°F. for 20 minutes.

The rubber latex reinforced in accordance with the method of this invention may be coagulated under controlled pH conditions to produce a product having different physical properties depending upon the pH condition used. For example, when the reinforced rubber latex is coagulated with, for example, a salt such as sodium chloride at a pH of at least 10, the rubber is recovered as a powdered rubber. The powdered form of the rubber greatly improves the processing thereof. When the reinforced rubber latex is coagulated at a pH of less than 7, the rubber is tacky whereas the product is dry and non-tacky when coagulated at a pH of from about 7 to about 10. The reinforced rubber is useful as a carbon black master-

batch for the manufacture of tread stock and ply stock for use in the construction of a pneumatic tyre.

#### WHAT WE CLAIM IS:—

1. A method of reinforcing natural or synthetic rubber in latex form, which comprises adding a reinforcing agent to a water soluble phenolic resin carrier compatible with both the reinforcing agent and the rubber component of the latex to form a pre-blend thereof, and adding the pre-blend, optionally after aging, to the rubber latex.

2. A method according to claim 1 in which compounding ingredients are present in the rubber latex.

3. A method according to claim 1 in which the reinforcing agent is carbon black and the carrier is a water soluble condensate of an aldehyde and a phenol.

4. A method of reinforcing rubber latex substantially as described in the foregoing Example.

5. Rubber latex reinforced in accordance with the method of any of the preceding claims.

6. An article formed by drying the reinforced rubber latex of claim 5 into a desired shape and then curing the dried shape.

7. Powdered rubber made by coagulating the rubber latex according to claim 5 at a pH of at least about 10.

8. Rubber carbon black made by coagulating the rubber latex according to claim 5 at a pH of between about 7 and about 10.

9. Carbon black reinforced rubber made by coagulating the rubber latex according to claim 5 at a pH of less than 7.

10. A method of forming a rubber tread on the carcass of a pneumatic tyre which comprises applying at least one layer of the rubber latex of claim 4 to the carcass of the tyre, drying the layer of latex and vulcanizing the dried layer into a wear resistant tread.

11. The method according to Claim 3 in which the aldehyde is formaldehyde and the phenol is resorcinol.

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