

PATENT SPECIFICATION (11)

1 421 012

1 421 012

- (21) Application No. 14993/73 (22) Filed 28 March 1973 (19)
(31) Convention Application No. 292 468 (32) Filed 26 Sept. 1972 in
(33) United States of America (US)
(44) Complete Specification published 14 Jan. 1976
(51) INT. CL.² C08C 1/14 C08J 3/16
(52) Index at acceptance
C3E 1D 1X
C3Q C12A C13A C14A C17 C6B C8C D1A S2 T1A



(54) PREPARATION OF NATURAL MASTERBATCHES

(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 latices. More particularly, it relates to the processing of natural rubber latices into commercial rubber crumb and products obtained thereby. Still more particularly, it relates to an improved process for coagulating natural rubber latices, either in white rubber or masterbatch form, into a readily acceptable and commercially described crumb.

In United States Patent Specification No. 3,108,983 there is disclosed a unique, and valuable technique for preparing synthetic rubber crumb from synthetic rubber latices, particularly of the butadiene-1,3 type. This process constituted a major step forward in the art by providing a successful technique for coagulating synthetic rubber latices either in their white (non-pigmented form) or in their pigmented (masterbatched) form without the use of a contaminating salt as a coagulation aid. The coagulated crumb so obtained by this technique has the requisite tack and particle size (preferably about $\frac{1}{4}$ to $\frac{3}{8}$ inches) to be commercially acceptable and valuable, and at the same time produces a synthetic rubber which has competitive strength and elongation properties.

Generally speaking, the process of this patented invention involves the coagulation of synthetic latices using a coagulation system in which acid is employed alone. It generally comprises bringing together a latex in an acid-coagulating system and subjecting the resultant mixture to concurrent agitating and comminuting actions. Upon completion of this coagulating, agitating and comminuting process, the resultant coagulant in the form of a crumb is separated, and

further processed in conventional equipment.

As disclosed in that patent, the process is applicable to a wide variety of synthetic rubber latices either in pigmented or unpigmented form. However, this invention as disclosed, is not applicable to the preparation of rubber crumb from natural rubber latices since, for some reason unknown at the time, natural rubber latices would not form commercially acceptable crumb when employing the techniques, parameters, and equipment disclosed in this aforementioned patent.

For many industrial and commercial end uses, particularly where the finished product is to be subjected to severe dynamic conditions, natural rubber still retains its place as the best elastomer. This is not to say, of course, that it is always the rubber actually employed. Users often compromise high physical qualities in order to obtain acceptable pricing levels, ready availability, economy, and the like. Thus mere adequate performance by a synthetic rubber can often favour its use despite the better physical properties of natural rubber. Thus one area in which a major contribution to the natural rubber art could be made, would be in economizing its production processes. For example, if one could develop a process for producing natural rubber crumb which had the requisite physical properties and yet was simple and economical to carry out, a large contribution to the natural rubber industry would be made since it would be competitive with synthetic rubbers of equal or poorer physical quality.

This problem and the need for new development have long been recognized in the art. The plantation industry for example has been very active in the last few years investigating alternative methods of processing natural rubber with the objective of producing a material which could be sold in commercially acceptable form at competitive prices. Arising out of this effort, several methods have been proposed for converting natural rubber latex first into a wet crumb and then into dry rubber. For example, United States Patent Specifications 100

Nos. 1,601,226; 1,623,517; 2,560,253; 2,769,795; 2,820,836-8; 2,980,639; 3,004,940; 3,048,559; 3,298,984; 3,335,200; and British Patent Specification No.

1,125,801, exemplify the methods which have been developed to render natural rubber and particularly natural rubber-carbon black masterbatching processes economically desirable. Unfortunately, these many prior art processes (some of which are intended to be applicable to both natural and synthetic rubber) involve such drawbacks as (1) the necessity of employing unfamiliar processing techniques which in turn necessitate the use of entirely new equipment and new training of personnel; (2) modifications of existing processes involving extensive and complicated mechanical and chemical treatments of one or more of the ingredients going into the rubber-carbon black masterbatch or into the rubber latices alone, or (3) serious limitations on their ability to handle successfully natural rubber, and produce a crumb and rubber commercially acceptable and competitive with those obtained by other techniques, particularly those which employ and produces synthetic rubber.

From the above it is clear that in assessing the desirability of any new method for preparing natural rubber alone or combining it with carbon black, several factors have to be borne in mind, and of these the important ones are: comparability of the costs with those for conventional processes; the ability to perform the process in existing equipment, as far as possible; whether the process is sufficiently versatile to deal with most or all forms of starting materials (field latex, scrap, etc), and how the properties of the final product compare with those of conventionally produced synthetic or natural rubber.

In light of the above background, it is evident that if in some way the basic, but valuable and unique techniques of United States Patent Specification No. 3,108,983 could be made applicable, and rendered adaptable to, natural rubber latices, a significant step forward in the art would be achieved. Not only would the need for complex new equipment be eliminated, but the economy of this patented technique would be transferred to natural rubber crumb, thus rendering it commercially competitive.

The present invention has been made with this in mind.

According to the present invention there is provided a process for preparing natural rubber crumb from a natural rubber latex which comprises heating the latex to a temperature above 50°C, contacting the latex during or after the heating with an acid capable of coagulating the latex, adding a cationic coagulating aid to the latex prior to or during contact with the acid and sub-

jecting the latex, acid and coagulating aid mixture to agitation and comminution for a period of time sufficient to form the crumb.

The present invention renders the valuable techniques of United States Patent Specification No. 3,108,983 applicable to the formation of commercially acceptable and competitive natural rubber crumb either in white form or masterbatched with carbon black. This is achieved, in part by the finding that what made natural rubber unworkable in the aforesaid patented system was the existence of a number of physical and chemical properties which inhibit the requisite degree of coagulation and which are not found in synthetic latices.

In this respect it was found that one of the major causes of improper coagulation was due to the presence of a certain combination of naturally occurring proteins, amino acids and other stabilizing materials and that such natural stabilizers generally comprised not only an anionic material (or materials) which is deactivated with an acid, but a heat sensitive material (or materials) possibly a type of albumin, which is deactivated by heating the latex to above about 50°C and a material (or materials), apparently most potent in fresh field latex, which is deactivated by a cationic material such as a high molecular weight polyamine. In addition to the above, it was further found that when carbon black as added to natural rubber latex in the normal manner (i.e. with heavy agitation), there was a distinct tendency for auto-coagulation to occur prior to entering the coagulation zone. This presented serious problems of clogging and undesirable particle sizes in the final crumb. On the other hand, it was found that the carbon black could be added in a sufficiently gentle manner to obtain a good mixing but to prevent auto-coagulation from becoming a problem.

An acid coagulant is, of course, employed in the technique of United States Patent Specification No. 3,108,983 and thus this technique is inherently geared to deactivate one of the three stabilizing factors in natural rubber latex. Acid, furthermore, has been a time-honored coagulant for natural rubber (to form a gell rather than a crumb of commercially acceptable particle size). Thus dealing with such a material is already a familiar technique to the art. The other factors, however, are not inherently built into the disclosed techniques of the aforementioned patent and this is now thought to be the reason why it was not applicable to natural rubber latices.

Generally speaking then, the subject invention comprises building into the basic operating techniques disclosed in United States Patent Specification No. 3,108,983 —

in an economical fashion — the necessary factors to destabilize sufficiently the natural rubber latex and — in the case of masterbatching — prevent auto-coagulation, thereby to achieve the desired results. Thus the subject invention generally comprises a process for preparing natural rubber from a natural rubber latex by heating the latex to a temperature above 50°C either prior to, or simultaneously with, adding to said latex an acid capable of coagulating the latex; subjecting the mixture to mechanical agitation and comminution for a period of time sufficient to form a crumb of the requisite particle size and collecting the wet crumb formed thereby.

The process as disclosed hereinabove, is readily adaptable to masterbatching by, in addition to the above steps, gently mixing a water slurry of carbon black material with the latex prior to coagulation, the degree of mixing being sufficiently great so as to provide an adequate dispersion of the carbon black in the latex, but at the same time insufficient to cause any substantial amount of auto-coagulation to occur.

The wet crumb so-formed and collected is then subjected to known techniques in the industry for producing the final product.

The natural latices useful as a starting material in the subject invention constitute all of the natural latices known and which are conventional in the art. Examples of such latices include: fresh field latex, evaporation concentrated natural latex, and centrifugally concentrated natural latex as well as mixtures of these with a limited amount of synthetic rubbers (i.e. up to about 50% by weight synthetic rubber). 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. The latex, as employed will preferably have a pH adjusted to a value greater than about 9.5. More preferably the pH value is in the range of from 9.5 to 11 and most preferably from 10.0 to 10.5.

In some natural latex systems, destabilization is sufficiently realized, by the use of an acid destabilizing agent (coagulating agent) and the heating of the latex to its destabilization point (above 50°C). In accordance with the present invention natural latex systems and particularly when employing fresh field latices, destabilization is achieved by the inclusion of a cationic coagulation aid (or by another name destabilization material) in order to achieve the requisite tack and crumb size.

The acid employed for coagulation may be any organic or mineral acid normally employed for this purpose in amounts and concentrations well known to those skilled

in the art. The pH maintained during coagulation is generally somewhat higher than those used for synthetic rubber latex coagulation, but it is maintained at an acidic level, being for the purposes of this invention usually of the order of about 4.0–6.5 and preferably 4.5 to 6.0. Examples of useful acids include acetic, formic, sulphuric, phosphoric and the like, and mixtures of such acids.

Where the natural rubber latex processed according to this invention is a diluted evaporation or centrifuge concentrated latex, the pH level in the coagulation zone determined by the addition of the acid coagulant is usually maintained at a level of 3.5 to 5.5 preferably 4.5 to 5.5. Similarly, where the natural rubber latex processed according to this invention is field latex, the pH level in the coagulation zone, determined by the addition of the acid coagulant, is maintained at 4.5 to 6.0.

The coagulation aid employed 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. These coagulation aids are used when coagulating fresh field latex and are when employing the other natural rubber latices. The amount employed will vary with the type of latex chosen, but generally 0.2 to 2.0 parts by weight (based upon the contained polymer content) is sufficient to achieve the degree of destabilization required.

Similarly as disclosed in United States Patent Specification No. 3,108,983, when carrying out the coagulation step of this invention, the intensity of agitation and comminution to which the latex is subjected generally will determine the particle size of the ultimate product. In general, it can be stated that the softer and stickier the coagulum normally is, the more intense the agitation and comminution must be to obtain the desired particle size. Non-pigmented latices thus usually require more intense agitation and comminution than do pigmented (e.g. carbon black) latices. Insufficiently or excessively intense actions in any particular case may be expected to lead to soft chunky coagulum and coagulum comprising considerable amounts of fines, respectively. The intensity of actions required for the treatment of any particular latex is not an easily definable measurement. It depends on the means employed to obtain the agitating and comminuting actions and the length of time the latex is subjected to such

actions in the particular means. For any particular coagulating device, however, the intensity and length of time of the agitating and comminuting actions necessary to obtain the desired results may be readily determined.

As stated above, one of the most important steps in rendering natural rubber latices useful in the aforesaid patented technique is the step of heating the latex to a temperature sufficient to desensitize the "albumin-type" stabilizing agents naturally present in the latex. For most latices this means heating the latex to a temperature above 50°C and preferably between 50 and 80°C. Time does not appear to be a critical factor, since a hold at these temperatures of anywhere from less than about 1 minute to an hour or more is found sufficient to achieve the desired results — the time actually employed being determined by routine experimentation once a specific type of latex is chosen for use.

The heating step may be carried out during the coagulation step. However, when producing white rubber it is preferred to carry it out prior to coagulation. In this respect, desensitization has been found to be non-reversible. Thus the latex may be heated in a holding tank and coagulation carried out economically at lower (e.g. ambient) temperatures. Likewise, the addition of the coagulation aid (e.g. polyamine) may be added during the coagulation step, but preferably is added after heating but before coagulation is effected.

While any suitable coagulation tank which provides the requisite degree of agitation and comminution may be employed, it is preferable to employ that equipment generally disclosed in United States Patent Specification No. 3,108,983 and set forth in Figure 3 of the accompanying drawings.

The invention will now be illustrated with reference to the accompanying drawings, in which:

Figure 1 is a flow sheet of certain preferred embodiments for carrying out the processes of this invention. It should be noted that included in this flow sheet, by way of broken lines, are two alternative processes within the scope of this invention;

Figure 2 illustrates a flow diagram of a particular preferred process according to this invention;

Figure 3 illustrates a particularly preferred coagulation zone as substantially disclosed in United States Patent Specification No. 3,108,983. The cutaway portion illustrates the preferred construction of the interior of the coagulation zone; and

Figure 4 is a flow diagram illustrating a unique and economical method of controlling the flow rate of natural rubber latex

and the carbon black slurry to the coagulation zone.

Referring to Figure 1, a natural rubber latex is prepared and stored in latex preparation and holding zone 1. A stabilizer can be added to the latex in zone 1, if necessary, but external stabilizers may not be necessary in the continuous process of this invention if the process is operated so as to consume the natural rubber latex virtually as fast as it is being prepared. On the other hand, if there is to be some "holding" in zone 1, it may be desirable to add external stabilizers to the natural rubber latex, in accordance with conventional techniques and practices in the art. It is also possible that the natural rubber latex chosen may be quite stable normally and thus not need the addition of external stabilizers.

The latex present in zone 1 should preferably have a total solids content of from about 16 to about 30%. The total solids content of the latex may be measured according to the following procedure: weigh aluminum drying pans on an analytical balance to the nearest milligram. Place not more than 1.5 to 2 grams of the latex into each of the pans and again weigh to the nearest milligram on the balance. The latex is dried in an oven at 160°C for no less than 12 minutes. The sample is then cooled and reweighed. The total solids content is determined by the following equation:

$$\% \text{ TSC} = \frac{\text{weight of dried sample}}{\text{initial weight of sample}} \times 100$$

A carbon black slurry is prepared and stored in the slurry zone or tank 2. If necessary, a stabilizer or emulsifier may be added to the carbon black slurry. The carbon black slurry preparation constitutes a significant aspect of the masterbatching processes of this invention in that pelletized or unpelletized carbon black (as received) may be introduced into the slurry zone 2 and mixed therein with water.

The slurry zone 2 is provided with a recycle line X which carries a portion of the carbon black slurry back into slurry zone 2 for a further pass through the centrifugal pumps Y. The recycle line X is so set up in relation to line Z which carries the slurry to the coagulation zone that there is provided by the recycle line an average residence time in the slurry zone 2 of at least about 2 hours. During this residence time, the numerous passes through the high speed centrifugal pump Y serve to grind continuously the raw carbon black, in addition to the grinding effect of the agitation means (not shown), which is normally provided in the slurry zone 2. Because of this unique step in the process, raw carbon

black, or pelletized carbon black may be reduced to the appropriate size, and thus made suitable for use according to the process of this invention without the use of any expensive and/or sophisticated equipment or external processing steps.

As stated above the carbon black slurries for use according to the process of this invention are preferably those which have a total solids content of from about 4.0 to about 7.5 percent by weight.

Determination of the percent total solids content of the carbon black slurry may be made according to the following procedure: weigh aluminum drying pans on the analytical balance to the nearest milligram. Place approximately two grams of the well-mixed slurry into each of the pans and again weigh to the nearest milligram on the balance. Add approximately one cc of acetone to each of the pans. The acetone should be added in such a manner that the slurry and acetone are spread evenly over the bottom of the pan. Dry the pans in an oven at 160°C for no less than 12 minutes. Cool the pans in a desiccator for about 3 minutes and reweigh. The percent total solids content is calculated according to the same equation used to calculate the total solids content of the natural rubber latex given hereinabove.

The natural rubber latex is pumped from the latex preparation zone 1 and the carbon black slurry is pumped from the slurry zone 2 simultaneously to a mixing zone designated by 5, wherein the latex and the carbon black slurry are briefly mixed. The mixing effected in mixing zone 5 may be merely by the normal agitation caused by pumping the two fluids together so as to be gentle enough such that with a short enough residency time in zone 5 (of the order of about 1 sec. to 2 minutes) no substantial amount of auto-coagulation occurs.

The problem of auto-coagulation can be essentially avoided altogether by use of one of the alternative processes illustrated in Figure 1 and designated by A and B. According to process A, the natural rubber latex and the carbon black slurry are pumped directly to the coagulation zone 6 and enter the coagulation zone in separate streams. According to the alternative process B, the natural rubber latex and the carbon black slurry lines are brought together into one line just prior to entrance into the coagulation zone 6. This process essentially avoids the problem of auto-coagulation while still providing some degree of mixing of the two streams prior to entrance into the coagulation zone 6.

Optionally, an anti-oxidant and/or an extender oil can be added to either the natural rubber latex, the carbon black slurry, or both prior to the mixing of the two

ingredients as is shown in Figure 1. The zone indicated by 4 serves to indicate the preparation zone of these additives. Obviously, if both additives are to be incorporated into the latex and/or the slurry, two zones may be employed, one for preparation of each of these two ingredients. The additive(s) may be carried from zone 4 also directly to mixing zone 5 rather than or in addition to the introduction of these additives into the latex line and/or the slurry line. The anti-oxidant and/or the extender oil are preferably prepared in zone 4 in the form of water emulsions.

Mixing or agitation means, while not shown in Figure 1, are preferable, if not required, in each of zones 1, 2 and 4.

The latex and the slurry are introduced into mixing zone 5, or alternatively directly into coagulation zone 6, in a typical latex to slurry ratio by weight of about 1:2; however, the ratio will depend on the desired amount of carbon black in the final product masterbatch. The ratio by weight of carbon black to natural polymer may range from about 1:1 to about 1:3 or even lower. The slurry to latex ratio will, of course, vary accordingly.

If processed through mixing zone 5, the mixture of latex and slurries proceed from it to the coagulation zone, designated by 6¹, where the ingredients are subjected to (1) a relatively high degree of agitation both to mix and comminute the product formed and (2) concomitant coagulation. The total solids content of the combined ingredients entering the coagulation zone is preferably in the range of from about 15 to about 18% by weight. The total solids content is calculated according to the method used to calculate the total solids content of the carbon black slurry. The latex and the slurry entering coagulation zone 6¹ (or alternatively by way of processes A and B, coagulation zone 6) are preferably under a positive fluid pressure to minimize any potential for clogging or plugging of the system due to any small amount of auto-coagulation that might have occurred.

Simultaneously with the addition of the latex and the slurry into the coagulation zone, an acid coagulant is introduced into coagulation zone 6¹ (or alternatively, coagulation zone 6) from the acid make-up zone 3. The acid is introduced into the coagulation zone in an amount sufficient to develop in said coagulation zone an acidic pH value (i.e. below 7.0). Preferably the pH value in the coagulation zone is in the range of from about 4.5 to about 6.0. The acid introduced into the coagulation zone from acid makeup zone 3 is introduced preferably in a concentration of from about 0.5% to about 2.0% by weight dependent upon the acid coagulant chosen.

6 15
A small amount of a cationic coagulation aid, preferably a polyamine as hereinbefore described, is added to this system. This is usually accomplished by adding it to the acid coagulant or it may be added as a separate solution into the coagulation zone. It is preferably added in the range of 5 to 10 parts-by-weight aid per 100 parts by weight acid (on a concentrated basis).

10 In order to destabilize the latex, coagulation zone 6¹ (or alternatively, coagulation zone 6) may be heated to above 50°C and preferably between 50°C and 65°C. Alternatively, the latex may be destabilized by preheating it in zone 1 to above 50°C. Then, in this embodiment the coagulation zone is not heated and coagulation is allowed to proceed. It has been found for purposes of masterbatching that heating in the coagulation zone is somewhat more preferred, while, as stated above, preheating is more preferred when producing white rubber.

15 As stated hereinabove, sufficient agitation and comminution must be provided for in the coagulation zone so that the individual crumbs formed do not tend to adhere together, which would cause the resulting particle size to be too large.

20 While any system may be employed which provides the necessary degree of agitation and comminution such as Cowles Dissolver (Cowles Dissolver Co.) or a Lightning Mixer (Mixing Equipment Co.) it is preferred to employ the device illustrated in Figure 3 and as generally disclosed in United States Patent Specification No. 3,108,983. The different feed orifices employed in this patent are equally as applicable as the one illustrated in Fig. 3. Thus no substantial difference exists between the two disclosed coagulators, the design of Fig. 3 being somewhat more preferred.

25 In operation and with reference to Fig. 3, the natural rubber latex and the carbon black slurry enter the coagulator 6 by way of line b. Just downstream from the point at which the latex and the slurry enter the coagulator, the acid coagulant is introduced by way of line a. Alternatively, the acid may be introduced further downstream in the coagulator or at several points along its length. The character of the crumb, in this respect, may be varied by altering the point of addition of the acid. Generally speaking, the nearer to the charge end the acid is added the larger the crumb will be.

30 If it is desired to destabilize the latex by heating the coagulation zone, this may be done by way of the introduction of steam into the coagulation zone through line c. The steam is preferably introduced at the charge end of the coagulator, as shown. More preferably, the steam is introduced just opposite the point of introduction of the acid, as shown.

70 The temperature imparted to the coagulation zone by way of the steam (or alternatively, by any other heating means) can be varied over a relatively wide range depending on the makeup of the blend of natural rubber latex and carbon black slurry introduced into the coagulation zone and the corresponding speed of coagulation of these two ingredients. The temperature may need to be increased towards the maximum range in order to insure the completion of the coagulation within the coagulation zone. It is most desirable to have the maximum temperature less than the temperature at which the natural rubber latex will degrade so as to produce the best of all possible products.

75 The mixing means or agitation means shown is a radially extending blade e mounted on a shaft d which is to be closely fitted inside the tubular coagulator, designated generally by 6. The angle of the blades e is set so as to provide a maximum cutting or chopping action on the ingredients during coagulation, as well as to provide for the forward advancement of the ingredients in the coagulation zone. This type of mixing means is described in United States Patent Specification No. 3,108,983. The speed of rotation of the agitation means is generally adjustable within the range of about 300 to about 1400 revolutions per minute (rpm). The speed of rotation of the agitating and chopping means can be adjusted upwardly to get a smaller rubber crumb or to handle a tougher stock of material. Where the latex used is fresh field latex, the speed of rotation should be in excess of about 600 rpm.

80 From the coagulation zone 6¹ (or alternatively, coagulation zone 6) the coagulated latex-carbon black mixture is preferably passed to a holding zone 7 where the crumb and mother liquor are held so as to insure that coagulation has been completed. Such a holding zone 7 preferably includes agitating means (stirrers, etc.) which will provide mild agitation and comminution such that any coagulum not completed in zone 6 or 6¹ and formed in zone 7 will be a crumb of the requisite particle size.

85 From the holding zone 7, the coagulum is carried forth through the further processing steps of screening, washing, pressing, rolling, grinding, shredding, etc. in any desired combination. In Figure 1, the coagulum is shown leaving holding zone 7 and being subjected to screening and dewatering in screening zone 8, washing in washing zone 9, a second screening and dewatering in screening zone 10, grinding and/or milling in zone 11, and shedding in zone 12.

90 After being subjected to these further processing steps in zones 8 to 12, or any 130

other combination of the processing steps discussed above, the coagulation latex-carbon black mixture is subjected to drying at a temperature high enough to dry the material yet below the temperature at which the latex will degrade. The drying temperature is preferably in the range of from 70°C to 80°C.

The latex-carbon black coagulum produced according to the process of this invention is preferably de-watered by screening and dried in the form of a rubber crumb material. However, other de-watering and drying procedures are within the scope of this invention. For example, the crumb could be subjected to rotary drum drying or the crumb could be de-watered in a filter press and subsequently dried. Other alternatives will be clear to one of ordinary skill in the art. As was previously stated, the drying temperature should be kept below the temperature at which the natural rubber will tend to degrade.

Referring now to Figure 2, this figure illustrates with more particularity a preferred process according to this invention. Illustrated herein is the use of both an extender oil and an antioxidant in the process. These additives are prepared in tanks 4 and 4¹, respectively. According to the process shown in this figure, both of these ingredients are introduced into the natural rubber latex line just prior to the mixing of the latex with the carbon black slurry at point M. The flow rates of the extender oil and the anti-oxidant are controlled by way of proportioning pumps designated by W. In this figure the agitation means for the latex preparation zone 1, the carbon black slurry zone 2, and the extender oil and antioxidant zones 4 and 4¹ are shown as conventional motor driven stirrers. These stirrers are designated by A¹.

Suitable extender oils for optional use according to the process include both the aromatic and naphthenic extender oils as well as the more highly aromatic oils. Such materials are known in the art. As discussed above, the extruder oil can be added to either the natural rubber latex line or to the carbon black slurry line or to both lines prior to coagulation in the coagulation zone. In addition, the extender oil may be added in the coagulator. The extender oil is preferably added into the process in the form of a water emulsion of a total oil content (i.e. TSC) of up to about 50% by weight. Preferably the water emulsion of the extender oil is adjusted to a pH level in the range of about 9.5 to about 11.0. The purpose of this is to insure maintenance of the pH level of the natural rubber latex, which pH level is very important in this process.

Antioxidant materials suitable for use in

the instant invention include such conventional antioxidants as a nonylated diphenylamine anti-oxidant sold by the Uniroyal Chemical Division under the trademark Poly-lite, N-alkyl-N-phenyl-β-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. Of course, any other suitable antioxidant may be used. 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% by weight. Preferably the pH of this water emulsion is, like the extender oil emulsion and for the same reason, in the range of from about 9.5 to about 11.0. The antioxidant is added, when used, in an amount of from about 1.0 to about 1.25 parts based on the weight of the natural rubber of the latex. The addition of antioxidant in excess of 1.25 is possible, but in many cases makes little or no further improvement in the properties of the resulting product.

According to this process, the regulation of the carbon black slurry and the natural rubber latex to the coagulator 6 is effected by magnetic flow meters such as the Foxboro Magnetic Flow Meters known in the art and sold by the Foxboro Company. The mixing of the carbon black slurry and the natural rubber latex according to the process of this figure is effected by joining the two feed lines as one at point M just prior to introduction of the ingredients into the coagulator 6. The valves illustrated in the figure and designated by C are over-flow valves which serve to permit flow through the flow meters while adjustments are being made just prior to starting the coagulation process.

A holding zone is illustrated herein as a tank 7. Tank 7 is provided with agitation means both to agitate and chop the coagulated latex-carbon black mixture discharged from the coagulator. The agitation means are designated herein by D. The motor used to drive the agitation means is preferably a more powerful motor than those used to drive the previously described stirrers, designated by A¹. This is necessarily due to the fact that the agitating means in tank 7 serves to agitate and comminute (coagulating latex not coagulated in zone 6) and to maintain the coagulum in a subdivided state. Suitable blades for effecting this dual purpose include a flat cutting-type blade such as that used in a Cowles

Dissolver sold by the Cowles Dissolver Co., Inc., marine type propeller blades, and the like, as well as the agitation means of the aforesaid United States Patent Specification No. 3,108,893. Of course, the use of any other type of blade or agitating means which has a significant degree of cutting effect is also within the scope of this invention.

From the holding zone 7, the crumb passes to a screen 8 where it is de-watered. From the screen, the crumb is delivered to a re-slurry or wash zone 9. Additional water is added herein to effect the washing of the crumb. From this washing zone 9 the coagulum is carried to further processing and drying.

Figure 4 is included to illustrate a highly economical method of flow control of the natural rubber latex and the carbon black slurry to the coagulation zone. This economic control is effected using wier boxes. The wier boxes are designated by numerals 100 and 101. These wier boxes are enclosed vessels provided with orifices 102 at or near the bottom of the enclosed vessel. The orifices are generally calibrated in various coefficients based on the flow rate in gallons per minute versus the liquid head in the enclosed tank. Once the initial makeup of the desired coagulum product is determined, the particular orifice chose for maintaining the proper flow rate to produce such a product is determined by going through a series of calculations known in the art.

The invention will now be illustrated with reference to the following Examples. Example 1 illustrates the production of white (i.e. nonpigmented) natural rubber crumb having commercially acceptable tack and particle size employing the equipment illustrated in Figure 3. Generally speaking the cylindrical shell has a length of about 2 ft. and an inside diameter of about 7 inches. A variable speed rotor extends along the axis of the shell carrying 11 sets of unpitched blades equidistantly spaced from each other. Examples 2 to 4 illustrate the preparation of natural rubber carbon black masterbatches according to the invention.

EXAMPLE 1

Fresh field latex is stabilized with ammonia and/or a caustic such as sodium hydroxide or potassium hydroxide so that the pH of the latex will be about 10.0 after heat destabilization. Other known stabilizing agents, anti-oxi-dants, and the like may also be added. The latex is then heated with steam to about 60—70°C and maintained at this temperature for about 1 hour. Thereafter a high polymeric weight polyamine such as Nalco 107 (Nalco Chemical Co.) Drewfax C-220 (Drew Chemical Co.)

or Polyamine H (Dow Chemical Co.) is added to the latex in an amount equal to about 0.2—2.0 parts based on the contained polymer. The latex is then pumped to the above-described coagulator where sulphuric acid is added to reduce the pH of the mixture to about 5.5 to 6.0. With the coagulator running at about 1000—1500 rpm, a dwell time of about $\frac{1}{2}$ minute produces an acceptably sized crumb of acceptable tack. The crumb is washed, and further processed in accordance with conventional techniques.

As stated hereinabove, this invention is also useful for making natural rubber masterbatches. As further stated, such a process generally comprises, in addition to the above-described steps, admixing carbon-black with the latex, prior to coagulation, and in a sufficiently gentle fashion to prevent any substantial amount of auto-coagulation from occurring.

What will constitute sufficiently gentle mixing will vary as different systems are employed. Generally speaking, however, mixing by merely flowing together in an inlet pipe rather than with overt stirrers sufficiently disperses the carbon black in the latex to form a substantially homogeneous dispersion of the carbon black in the final crumb, but is insufficient to cause auto-coagulation. In this respect, gentle mixing is somewhat time dependent. That is to say, the less gentle the mixing the more swiftly the mix should be subjected to the acid coagulum and the initiation of coagulation, agitation and comminution. With ordinary pipe inlet mixing it is usually sufficient to subject the mix to coagulation within a few seconds thereafter to prevent auto-coagulation from occurring.

The carbon black employed in this process may be any of the well-known carbon blacks conventionally used in the art. Such carbon blacks include all conventional types of furnace and channel blacks prepared for rubber compounding. Preferably they are mixed with the latex in the form of an aqueous slurry which preferably has a total solids content in the range 4 to 7.5% by weight. Preferably the pH of the carbon black slurry is substantially the same as that of the natural latex, and most preferably the particle size of the carbon black will be such that 99% or greater of the particles will pass through a 325 mesh screen (U.S. sieve size).

This masterbatching process is readily carried out in the apparatus disclosed in the aforementioned United States Patent Specification No. 3,108,983. In fact, the use of such equipment constitutes a preferred mode of carrying out the subject invention.

EXAMPLE 2

Fresh field natural latex suitably stabi-

lized, i.e. with ammonia, is diluted with water to a total solids content of 18.9% by weight.

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% by weight solids. The carbon black is reduced to a 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 found to be 5.2% by weight.

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% by weight.

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% by weight.

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	TSC or Concentration of Fluid	Equivalent Fluid
30	Latex	100	18.9%	529
	Carbon Black	50	5.2%	1921
35	Oil	10	48.7%	20.53
	Antioxidant	1.25	20.4%	6.18
		161.25		

40 The various fluids are now supplied by Foxboro Magnetic Flow Meters and proportioning pumps, as discussed above, and in the proportions indicated by the recipe to a high shear coagulator such as an Ashland coagulator as in United States Patent Specification No. 3,108,983 and described hereinabove.

45 The volume of the coagulator is 4 gallons with a throughput of 6.5 gal/min and a residence time of about $\frac{1}{4}$ 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 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.

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

55 The effluent from the coagulator is found to consist of a masterbatch crumb of between about $\frac{1}{8}$ — $\frac{3}{8}$ inch 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. The effluent is allowed to fill a holding tank and is subjected to moderate agitation after which it is washed, dewatered and dried in a circulating air oven at around 80°C.

EXAMPLE 3

60 Example 2 is again repeated except that the metered fluids are conducted to a tank fitted with baffles and an agitator such as a high speed Lightnin Mixer, sold by Mix-

ing Equipment Co., or a Cowles Dissolver. Steam is introduced into the tank to raise the temperature to 60 to 65°C. Acid-coagulation aid solution is added to the tank to a pH of 5.0 to 5.5.

Most of the crumb is found to be of moderate size but there is an appreciable quantity of very fine material that would be difficult to recover. Overall, however, the product is acceptable and of good quality.

EXAMPLE 4

Example 2 is again repeated except that fifty parts of FEF carbon black sold under the trade designation N-550 by Ashland Chemical Company is used in place of the N-219 carbon black. FEF is characterized by having less surface area per unit of weight than the N-219 black used previously. The crumb in the effluent is found to be large and the serum is clear. Under mild agitation in the holding tank, as used for the N-219 black, the crumb tends to ball up in the coagulation tank. This difficulty is found to be avoided if a higher speed agitator with a chopping or comminuting type blade such as in Fig. 3 is used.

The product is of moderate size and of acceptable high quality when there is provided an increased agitation in the holding tank.

The masterbatches prepared according to the process of the present invention have exhibited properties in finished products at least equal to and in many cases improved over the properties of the rubber products prepared in the usual manner. Thus, by using the improved process of the present

invention one gains not only the economic advantages of the process listed earlier, but also a product of a quality at least equal to and in many cases better than the materials or products conventionally and presently produced.

Several advantages other than economy are achieved by successfully adopting the basic patented technique to the production of natural rubber, either white or masterbatched, in accordance with the processes in the product (over other products process of natural rubber masterbatching according to the present invention offers all of the advantages of synthetic rubber or synthetic rubber masterbatches, along with the additional advantage of reducing cold flow of the product (because of the use of natural rubber) which in turn results in reduced packaging costs of the product. Improved aging and crack-resistance properties in the product (over other products produced by the known processes for natural rubber) are realized because the subject process now provides a reduced 'heat history' of the rubber compounds in the sense that since no smoked sheets are employed, the necessity of breaking down these sheets with high heat and mechanical working is eliminated. Furthermore, the rubbers and masterbatches produced by the processes of the present invention can often be compounded in one pass through a Banbury or roll mill while raw natural rubber must normally be first masticated and then compounded on at least two passes through a Banbury or roll mill. In addition, the improved processes of the present invention facilitate the preparation of a natural rubber product of such a uniform and reproduceable quality that the natural rubber can now be used in industries and for products which heretofore could not use natural rubber products because of their crude preparation and the lack of reproduceability of the desired qualities. In addition to these advantages is the commercially important fact that the crumb produced by this invention usually has a particle size of about $\frac{1}{4}$ to $\frac{3}{4}$ inches with less than 1% of the crumb passing through a 100 mesh screen (U.S. sieve size).

The process and products of the present invention are also useful for the preparation of extended natural rubber latex blends as disclosed in our copending Patent Application No. 1,4991/73 (Serial No. 1,421,011).

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

60 WHAT WE CLAIM IS:—

1. A process for preparing natural rubber crumb from a natural rubber latex which comprises heating the latex to a temperature above 50°C, contacting the latex during or after the heating with an

acid capable of coagulating the latex, adding a cationic coagulating aid to the latex prior to or during contact with the acid and subjecting the latex, acid and coagulating aid mixture to agitation and comminution for a period of time sufficient to form the crumb.

2. A process as claimed in Claim 1 in which the crumb has a particle size of $\frac{1}{4}$ to $\frac{3}{4}$ inches and less than 1% passes through a 100 mesh screen (U.S. sieve size).

3. A process as claimed in Claim 1 or Claim 2 in which the latex is heated to above 50°C prior to contact with the acid.

4. A process as claimed in any of Claims 1 to 3 in which the latex is fresh field latex.

5. A process as claimed in any preceding claim in which the cationic coagulation aid is a polyamine.

6. A process as claimed in any preceding claim in which the cationic coagulation aid is added in an amount from 5 to 10 parts by weight per 100 parts by weight of the acid.

7. A process as claimed in any preceding claim in which the cationic coagulation aid is added in an amount of 0.2 to 2.0 parts by weight based upon the total polymer content.

8. A process as claimed in any preceding claim in which sufficient acid is added to the latex such that the pH of the resulting mixture is in the range 4.0 to 6.5.

9. A process as claimed in any preceding claim in which the latex is heated to a temperature in the range 50 to 80°C prior to contacting the latex with the acid.

10. A process as claimed in Claim 9 in which the latex and acid are subjected to mechanical agitation and comminution at ambient temperature.

11. A process as claimed in Claim 1 which further includes admixing a particulate carbon black with the latex prior to contact with the acid, the admixing being sufficiently gentle to prevent the occurrence of any substantial amount of autocoagulation.

12. A process as claimed in Claim 11 in which the carbon black is of a particle size such that at least 99% of the carbon black will pass through a 325 mesh screen (U.S. sieve size).

13. A process as claimed in Claim 11 or Claim 12 in which the carbon black is in the form of a slurry having a total solids content in the range 4 to 7.5% by weight.

14. A process as claimed in any of Claims 11 to 13 comprising preparing the carbon black slurry in a slurry production zone, bringing together the slurry and latex to disperse the carbon black in the latex, but with sufficiently gentle mixing to prevent any substantial amount of autocoagulation, passing the latex and slurry to a coagulation zone while simultaneously



invention one gains not only the economic advantages of the process listed earlier, but also a product of a quality at least equal to and in many cases better than the materials or products conventionally and presently produced.

Several advantages other than economy are achieved by successfully adopting the basic patented technique to the production of natural rubber, either white or masterbatched, in accordance with the processes in the product (over other products process of natural rubber masterbatching according to the present invention offers all of the advantages of synthetic rubber or synthetic rubber masterbatches, along with the additional advantage of reducing cold flow of the product (because of the use of natural rubber) which in turn results in reduced packaging costs of the product. Improved aging and crack-resistance properties in the product (over other products produced by the known processes for natural rubber) are realized because the subject process now provides a reduced 'heat history' of the rubber compounds in the sense that since no smoked sheets are employed, the necessity of breaking down these sheets with high heat and mechanical working is eliminated. Furthermore, the rubbers and masterbatches produced by the processes of the present invention can often be compounded in one pass through a Banbury or roll mill while raw natural rubber must normally be first masticated and then compounded on at least two passes through a Banbury or roll mill. In addition, the improved processes of the present invention facilitate the preparation of a natural rubber product of such a uniform and reproduceable quality that the natural rubber can now be used in industries and for products which heretofore could not use natural rubber products because of their crude preparation and the lack of reproduceability of the desired qualities. In addition to these advantages is the commercially important fact that the crumb produced by this invention usually has a particle size of about $\frac{1}{8}$ to $\frac{3}{8}$ inches with less than 1% of the crumb passing through a 100 mesh screen (U.S. sieve size).

The process and products of the present invention are also useful for the preparation of extended natural rubber latex blends as disclosed in our copending Patent Application No. 1,4991/73 (Serial No. 1,421,011).

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

WHAT WE CLAIM IS:—

1. A process for preparing natural rubber crumb from a natural rubber latex which comprises heating the latex to a temperature above 50°C, contacting the latex during or after the heating with an

acid capable of coagulating the latex, adding a cationic coagulating aid to the latex prior to or during contact with the acid and subjecting the latex, acid and coagulating aid mixture to agitation and comminution for a period of time sufficient to form the crumb.

2. A process as claimed in Claim 1 in which the crumb has a particle size of $\frac{1}{8}$ to $\frac{3}{8}$ inches and less than 1% passes through a 100 mesh screen (U.S. sieve size).

3. A process as claimed in Claim 1 or Claim 2 in which the latex is heated to above 50°C prior to contact with the acid.

4. A process as claimed in any of Claims 1 to 3 in which the latex is fresh field latex.

5. A process as claimed in any preceding claim in which the cationic coagulation aid is a polyamine.

6. A process as claimed in any preceding claim in which the cationic coagulation aid is added in an amount from 5 to 10 parts by weight per 100 parts by weight of the acid.

7. A process as claimed in any preceding claim in which the cationic coagulation aid is added in an amount of 0.2 to 2.0 parts by weight based upon the total polymer content.

8. A process as claimed in any preceding claim in which sufficient acid is added to the latex such that the pH of the resulting mixture is in the range 4.0 to 6.5.

9. A process as claimed in any preceding claim in which the latex is heated to a temperature in the range 50 to 80°C prior to contacting the latex with the acid.

10. A process as claimed in Claim 9 in which the latex and acid are subjected to mechanical agitation and comminution at ambient temperature.

11. A process as claimed in Claim 1 which further includes admixing a particulate carbon black with the latex prior to contact with the acid, the admixing being sufficiently gentle to prevent the occurrence of any substantial amount of autocoagulation.

12. A process as claimed in Claim 11 in which the carbon black is of a particle size such that at least 99% of the carbon black will pass through a 325 mesh screen (U.S. sieve size).

13. A process as claimed in Claim 11 or Claim 12 in which the carbon black is in the form of a slurry having a total solids content in the range 4 to 7.5% by weight.

14. A process as claimed in any of Claims 11 to 13 comprising preparing the carbon black slurry in a slurry production zone, bringing together the slurry and latex to disperse the carbon black in the latex, but with sufficiently gentle mixing to prevent any substantial amount of auto-coagulation, passing the latex and slurry to a coagulation zone while simultaneously



passing the acid coagulant to the coagulation zone, mixing the slurry, latex and acid from the instant the slurry, latex and acid are brought together in the coagulation zone so as to agitate and comminute the latex and slurry, coagulation of the latex and slurry being substantially completed in the coagulation zone, and passing the coagulated latex carbon black mixture to a holding zone in which the coagulation is completed under agitation.

15. A process as claimed in Claim 14 in which the mixing of the carbon black and latex is effected by bringing the slurry and latex together just prior to passage into the coagulation zone.

16. A process as claimed in Claim 14 or claim 15 in which a portion of the slurry is recycled through the slurry production zone in such a manner as to provide an average residence time in the slurry production zone of at least 2 hours.

17. A process as claimed in any of Claims 13 to 16 in which the total solids content of the latex and the carbon black slurry is from 15 to 18% by weight.

18. A process as claimed in any preceding claim in which the latex has a total solids content of natural rubber in the range of from 16 to 30% by weight in which the pH of the latex is greater than 9.5.

19. A process as claimed in Claim 18 in which the pH of the latex is in the range of 9.5 to 11.0.

20. A process as claimed in any preceding claim in which the acid is added to the latex such that the pH of the resulting mixture is in the range 4.5 to 6.0.

21. A process as claimed in any preceding claim in which the acid added to the latex is of a concentration of from 0.5% to 2.0% by weight.

22. A process as claimed in any preceding claim in which the acid is sulphuric acid, acetic acid, phosphoric acid, formic acid, or mixtures thereof.

23. A process as claimed in any preceding claim in which an antioxidant is added to the latex, and/or to the slurry, when present, prior to contact with the acid.

24. A process as claimed in Claim 23 in which the antioxidant is added in the form of a water emulsion of a total solids

content of up to 20% by weight and of a pH in the range of 9.5 to 11.0.

25. A process as claimed in any preceding claim in which the natural rubber latex is field latex, diluted evaporation concentrated natural latex or diluted centrifuge concentrated latex.

26. A process as claimed in Claim 25 in which the latex is a diluted evaporation or centrifuge concentrated latex and in which the acid is added to the latex such that the pH is maintained at 3.5.

27. A process as claimed in Claim 25 in which the latex is field latex and in which acid is added to the latex such that the pH is maintained at 4.5.

28. A process as claimed in any preceding claim in which an extender oil is added to the latex, and/or to the slurry, when present, prior to the addition of the acid.

29. A process as claimed in Claim 28 in which the extender oil is in the form of a water emulsion of a total solids content of up to 50% by weight and a pH in the range of 9.5 to 11.0.

30. A process as claimed in any preceding claim in which the natural rubber crumb is subjected to the processing steps of washing, screening, pressing, rolling, grinding and shredding in any combination.

31. A process as claimed in any preceding claim in which the natural rubber crumb is dried at a temperature of from 70°C to 80°C.

32. A process for preparing natural rubber crumb from natural rubber latex substantially as herein described with reference to any of the Examples.

33. A process for preparing natural rubber crumb from natural rubber latex as claimed in Claim 1 substantially as herein described with reference to the accompanying drawings.

34. Natural rubber crumb when produced by a process according to any of Claims 1 to 33.

For the Applicants,
LLOYD WISE, BOULY & HAIG,
Chartered Patent Agents,
Norman House,
105—109 Strand,
London, WC2R 0AE.