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PATENT SPECIFICATION

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The inventor of this invention in the sense of being the actual deviser thereof within the meaning of Section 11A of the Patents and Designs Acts, 1907 to 1938 is JAN WILLEM VAN DALLEN, subject of the Queen of the Netherlands, J. P. Coenweg, No. 3, Buitenzorg, Java, Netherlands East Indies.

COMPLETE SPECIFICATION

Improved Manufacture of Rubber Powders and Rubber Dispersions

We, CENTRALE VERENIGING VOOR HERSTEL VAN PROEFSTATIONS VOOR DE OVERHEERSCHE CULTURES IN NEDERLANDSCH-INDIË, a Netherlands East Indian body corporate, of Batavia, Java, Netherlands East Indies, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:

The invention relates to a process for the preparation of a rubber powder from latex.

Several processes are already known in which from latex rubber can be obtained in granular, crumbly or powdery form.

These known processes can be divided in three groups, namely:—

1. Processes in which latex is atomised in a drying atmosphere. Although the rubber powder obtained in this way sticks less readily by adding certain substances to the latex which is to be atomised, a film of non-sticking substances can be formed round every rubber particle during the drying operation. Any further reducing by grinding or rolling the powder obtained in this way is impossible or hardly possible.

2. Processes in which drops of latex are caught on a moving surface, each drop being dried separately to a rubber particle, which particles are removed from the moving surface, if necessary after having been sprinkled with a substance which prevents sticking of the rubber. Any further reducing by grinding or rolling the crumbs or grains obtained in this way is impossible or hardly possible.

3. Processes in which the latex used as starting material is converted into a granular non-coherent coagulum or flocculate, which after being separated by passing through a sieve or centrifuging is dried to crumbs or grains. Quite different processes are known to obtain a granular non-coherent coagulum. On the one hand this can be performed by adding to the latex large quantities of certain solid substances and coagulating subsequently, on the other hand it can be obtained by subjecting the latex to certain chemical reactions, as for example the reaction with sodium nitrite.

All of these processes present difficulties.

If namely a large proportion of solid substances is added to the latex, a material is obtained containing only a small amount of rubber, which is a handicap for several applications; it is true that such materials, containing only a small quantity of rubber, can be ground, but they yield a fine powder with a poor rubber content.

It is impossible or about impossible to grind the modified rubber obtained by reaction with sodium nitrite, or further when it is dry, so that the fineness of the particles is determined almost exclusively by the size of the particles in the original coagulum.

Therefore the known processes for preparing rubber powder give either a granular or crumbly powder which cannot, or can hardly be further reduced, or powders which it is true can further be ground if necessary, but which always have a poor rubber content. The known rubber grains, crumbs or powders present therefore serious drawbacks.

According to the present invention it is possible to get a rubber powder, which contains a very small amount, at the most 5% of added solid substances and which, if necessary, can further be reduced by grinding until the size of the particles is equal to that of the original rubber particles in the latex. The powder prepared in this way is not in the least sticky and is not affected by moulds, bacteria or moisture, and in consequence of these extraordinary properties, it can be shipped in bales.

In order to obtain this result, sulphur or other vulcanising agent, zinc oxide or

other activator of the vulcanising agent and one or more stabilisers are added to the latex, after which either the mixture is left alone for a long period or to accelerate the reaction the mixture is heated. During this period the reaction is investigated at intervals either by desiccating small samples of the mixture or coagulating and measuring its tensile strength or by coagulating these samples in a known way, for example by adding acid, after which the coherence of the coagulum is determined each time. The surprising effect is then observed that the tensile strength of the films decreases gradually, while the coherence also diminishes. Finally a moment is reached when the tensile strength of the film becomes zero, or at least very small, while the second test also shows that the coherence of the coagulum has disappeared. At this moment the reaction is stopped in order to proceed to the separation of the rubber from the liquid.

This separation can be performed in several ways, for example by coagulation, by means of acids or salts or in any other known way, after which the powdery coagulum is separated from the liquid by filtration or centrifuging or in another way.

A second method of carrying out this operation is to pour out the liquid in thin layers, to permit the water to evaporate and to disintegrate the films obtained in this way, for example by grinding.

It is also possible to separate the rubber as a dry powder by spraying or atomising the liquid in a drying atmosphere.

Finally it is also possible to allow the ready latex mixture to trickle upon a moving surface and then to desiccate it on this surface.

By also adding vulcanising accelerators to the latex the process can be accelerated, or performed at a lower temperature.

As far as needed, fillers, or so-called softeners, or anti-oxidants or colorants or odorants or means to raise or to reduce the viscosity or the surface tension can also be added to the latex, separately or together.

The best results are obtained if the latex is fresh.

However, latices which have been highly purified by alternate creaming and diluting give normal vulcanisation products.

It has been known for a long time, for example from Patent No. 193,451, to vulcanise latex. During this process, however, the vulcanisation conditions are always chosen in such a way that the vulcanisation is complete or at least has proceeded so far that the final product obtained by coagulation or by desiccation by evaporation has a sufficiently high tensile strength.

It is not yet possible to explain definitely the theory underlying the invention or the nature of the rubber obtained. It may be possible that this is a question of a state, lying between the unvulcanised and the vulcanised states, which is obtained by performing the vulcanisation process like a slow motion picture, which is stopped at a certain moment. However, it is also possible that in this case a rubber product is obtained which is not vulcanised in the sense hitherto attached to this word. The sulphur compound, which is formed during the heating of the latex mixture or during the time it is left at rest, would in that case have a different character from that obtained under normal vulcanisation conditions.

More or less in accordance with the foregoing, the rubber film applied according to the invention has not the coherence and the tensile strength, nor the reduced solubility in rubber solvents, of vulcanised rubber, but on the other hand has the greater resistance to temperature variations and the reduced adhesive properties which rubber acquires as a result of vulcanisation.

In accordance with the above-mentioned hypotheses is also the fact, shown by chemical analysis, that the new form of rubber contains combined sulphur, but also is capable of normal vulcanisation. This can be obtained by heating the very delicate rubber film, obtained by the process according to this invention, for some time at vulcanisation temperature. In this way it acquires a high tensile strength, as appears from the experiment described below.

As the treatment and heating of the latex mixture according to the invention does not lead to a vulcanised rubber, the latex mixture heated in this way cannot be called a vulcanised latex in the sense which has hitherto been attached to this word.

Substances which are present in the resulting rubber powder and which are for any reason undesirable, can be removed in a physical or chemical way.

If the rubber powder, obtained according to the invention, is dispersed in water or an aqueous liquid, for example a salt solution, which can be effected easily in any mixing apparatus, a ball mill being particularly suitable, an artificial latex is obtained in which, on microscopic investigation, particles are found of the size of the original latex particles. This method of preparing an artificial latex

yields the possibility of greatly economising the transport costs of latex.

Also it is very easy to disperse the rubber powder, prepared according to the invention, in a rubber solvent, thus obtaining a dispersion which on microscopic inspection appears to consist of rubber particles of the original latex, but in a swollen state. It is remarkable that the swollen particles are not sticky; on pulverising the particles, a non-sticky paste is obtained of a very high rubber concentration.

By applying the new process to a latex mixture containing at least 20 parts of sulphur to 100 parts of rubber, a powder is obtained which can be used as an ebonite press powder or moulding powder. Additional heating of the powder produces an ebonite mass, which has practically no coherence and therefore is very easily disintegrated to a so-called ebonite powder.

These methods of preparing ebonite moulding powder or ebonite powder are simpler than the known methods, and moreover a separate mixing with sulphur powder has become superfluous.

If the rubber powder is formed by coagulation of the pre-treated latex mixture, it is advisable to perform this coagulation with salts or in a mechanical way, for example by stirring or shaking very quickly, so as to preserve the vulcanisation accelerator, which ordinarily is affected by acids.

EXAMPLE 1.

The starting material employed was a one day old Hevea plantation latex to which ammonia was added immediately after tapping.

Analysis of the latex gave:

Dry rubber content 35.9%

Total dry substance content 38.8%

Ammonia content 1.3 grams per litre

From this latex a mixture was compounded which contained per 100 parts rubber:

1 part of zinc oxide,

2 parts of sulphur, and

1 part of the vulcanisation accelerator "Vulcator SDC".

These chemicals were ground in a ball mill for 12 hours, while to the said 4 parts of mixture were added:

2 parts of a 10% ammonia-caseinate solution, and

6 parts of water.

This dispersion of chemicals was added to the latex while stirring thoroughly.

The latex mixture was then heated to a temperature of 80° C. during increasing periods, at the end of which each time in one portion of the latex mixture the structure of the coagulum was determined, which was effected by addition of formic acid, while another portion was poured out each time on horizontal glass plates. On desiccating by evaporation at normal tropical temperature (26°—30° C.) films were obtained on the glass plates, and the tensile strength at rupture, the elongation at rupture, and the stiffness (the tensile strength to effect an elongation of 600%) of the films were determined on a stretching machine (all measured in kilograms per cm²).

The results were as follows:—

TABLE No. 1.

Test	Duration of heating	Structure of the coagulum	Stiffness of the film	Tensile strength at rupture	Elongation at rupture in %	% combined S calculated on dry rubber
a	not heated	normal	7	25	982	0.5
b	1 hour	normal	5	20	1090	0.6
c	2 hours	normal	13	29	833	0.7
d	3 hours	coherent but non-elastic	—	12	505	1.0
e	4 hours	granular, non-coherent	—	7	223	1.4
f	5 hours	granular, non-coherent	—	0	0	1.6

From test *c* a rubber is obtained by desiccating as well as by coagulation, which cannot be ground to a powder without a very great consumption of energy. From test *d* a rubber is obtained, which, when wet, can be comminuted with a moderate consumption of energy. From test *e* a powder is separated by filtering the granular coagulum, then drying it and passing the dry powder through a heating mill. The films obtained from test *e* by desiccation by evaporation can very easily be ground, for example in a meat mill or a mill comprising crosswise arranged beating means.

In order to prove that the rubber obtained from test *e* is not vulcanised in the normal sense of the word, the films, which during this test had been obtained by desiccation by evaporation, were heated for increasing periods to 110° C. and to 150° C. After this additional heating the tensile strength was determined once more; these data are collected in table No. 2.

TABLE No. 2.

Heating: Temp.	Heating: Duration in minutes	Stiffness	Tensile strength at rupture	Elongation at rupture
110° C.	15	36	178	813
,,	60	35	177	802
,,	90	39	179	817
,,	135	32	192	836
,,	180	35	186	851
150° C.	5	27	213	943
,,	15	15	212	1068
,,	20	16	206	1062
,,	25	14	170	1073
Unheated film		—	7	223

EXAMPLE 2.

In order to show that the desired effect is also obtainable by leaving the latex mixture at rest at normal temperature, the following tests can be effected, in which a mixture with about the same composition as that of the mixture above described was kept for 28 days at ordinary temperature, after which a brittle state of the rubber film was attained. Tests made during that period gave the following results:

TABLE No. 3.

Days kept	Free S in latex per total dry material	Mechanical stiffness while stretching 630%	Properties of the Film: Tensile strength at rupture	Properties of the Film: Elongation at rupture
0	1.9	—	—	—
1	1.9	2	3	896
2	1.9	4	12	984
3	1.8	6	20	970
4	1.8	8	31	982
5	1.8	10	38	971
7	1.8	15	41	904
10	1.5	20	44	840
14	1.3	21	36	723
21	1.0	26	29	625
28	not determined ; film is brittle			

After 28 days the free sulphur was determined in the film, while moreover the films were submitted to some other vulcanisation tests, after which also the free sulphur was determined. The results are collected in the following table:

TABLE No. 4.

Age of the latex mixture	Minutes vulcanised at 90° C.	Free sulphur in the rubber %	PROPERTIES OF THE FILM Tensile strength at rupture	MECHANICAL PROPERTIES OF THE FILM Elongation at rupture
28 days	—	0.76	brittle	brittle
28 „	20	0.50	93	640
29 „	45	0.35	165	615
30 „	90	not determined	152	628
33 „	—	0.69	—	—

EXAMPLE 3.

As starting material a latex was taken which had been tapped the same day and which on analysis appeared to have the following properties:

Dry rubber content 40%
Total dry substance content 42.9%
Ammonia content 6.1 grams per litre.

From this latex a mixture was prepared containing per 100 parts rubber:

Zinc oxide - - - - 2.0 parts
Sulphur - - - - 40.0 parts
Vulkacit P extra N - - 0.8 parts

The dispersion of the chemicals was made in the same way as described in Example 1.

The mixture of latex and chemicals was heated until in a sample, a granular non-coherent coagulum was formed on coagulating with formic acid. Then the whole mass of the mixture was coagulated by addition of a solution of aluminium chloride. No real coagulation took place, but a highly viscous dispersion of flocculated particles was formed. As the size of the particles was so small that centrifuging or filtering presented difficulties, the mixture was desiccated in a vacuum oven. In this way an ebonite moulding powder was formed which could be easily ground still further. Thereupon the dry moulding powder, without application of pressure, was further vulcanised by heating it for 2 hours at 150° C., through which after some disintegration an ebonite powder was formed, which was sifted immediately. Each sieving fraction could very easily be disintegrated still further.

The fine rubber powder obtained according to the new process is applicable advantageously for mixing with asphalt for road purposes; it furnishes a good raw material for the preparation of rubber derivatives, and it can also be applied, for example, in the form of ebonite moulding powder or ebonite powder, to the manufacture of pressed and moulded articles, for which purpose the powder can be used alone or mixed with other substances, for example, synthetic resins.

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

1. A process for the preparation of a rubber powder from latex, characterised in that sulphur or other vulcanising agent, zinc oxide or other activator of the vulcanising agent, and one or more stabilisers are added to the latex; the mixture is left alone for a long period, or, if desired, to accelerate the reaction, the mixture is heated; during this period the condition of the mixture and of the rubber is examined at intervals either by desiccating small samples to a film and measuring its tensile strength or by coagulating the samples in a known way, for example by adding acid, after which the coherence of the coagulum is determined, and at the moment when in the first case the tensile strength has practically disappeared, or at least has become very small, or in the second case the coherence of the coagulum has vanished, the treatment of the mixture is stopped and the rubber is separated from the liquid.

2. A process as claimed in Claim 1, characterised in that the rubber is separated from the liquid by coagulation.

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2. A process as claimed in Claim 1, characterised in that the rubber is separated from the liquid by coagulation,

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for example by addition of acid, after which the powdery coagulum is separated from the liquid, for example by filtration or centrifuging.

3. A process as claimed in Claim 1, characterised in that the rubber is separated from the liquid by pouring out the liquid in thin layers, evaporating the water and forming films which can be disintegrated, for example by grinding.

4. A process as claimed in Claim 1, characterised in that the rubber is separated from the liquid by spraying or atomising the liquid in a drying atmosphere.

5. A process as claimed in Claim 1, characterised in that the rubber is separated from the liquid by allowing the liquid to trickle on a moving surface and desiccating it on this surface.

6. A process as claimed in any of the preceding claims, characterised in that, in addition, one or more vulcanisation accelerators are added to the latex.

7. A process as claimed in any of the preceding claims, characterised in that fillers, so-called soft-ners, anti-oxidants, colorants, odorants or agents for raising or reducing the viscosity or the surface tension are added to the latex separately or together.

8. A process for making a rubber dispersion having the character of an artificial latex, characterised in that the rubber powder prepared by the process claimed in any of the preceding claims is dispersed in water or in an aqueous liquid, for example a salt solution.

9. A process for making a non-sticky, water-free rubber dispersion, characterised in that the rubber powder prepared by the process claimed in any of Claims 1—7 is dispersed in a rubber solvent.

10. A process as claimed in any of Claims 1—7 applied to the manufacture of an ebonite press powder, characterised in that zinc oxide and, at least, 30% preferably about 40% of sulphur calculated on the dry rubber, are added to the latex.

11. A process for making ebonite powder, characterised in that the ebonite press powder prepared by the process claimed in Claim 10 is further heated for some time and the resulting mass is disintegrated if necessary.

12. A rubber powder when prepared by the process claimed in any of claims 1—7.

13. An aqueous rubber dispersion when prepared by the process claimed in claim 8.

14. A non-sticky, water-free rubber dispersion when prepared as claimed in Claim 9.

15. An ebonite press powder when prepared by the process claimed in Claim 10.

16. An ebonite powder when prepared by the process claimed in Claim 11.

17. The processes for the preparation of rubber powder and rubber dispersions substantially as described.

Dated this 14th day of December, 1938.

MARKS & CLERK.

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