

ALIEN PROPERTY CUSTODIAN

MANUFACTURE OF RUBBER POWDERS, RUBBER DISPERSIONS, EBONITE POW- DERS AND THE LIKE

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

Several processes are already known in which from latex rubber can be obtained in granular, 5 crumbly or powdery form.

These known processes can be divided in four groups, namely:

1. Processes in which latex is atomised in a drying atmosphere. Although the rubber powder 10 obtained in this way sticks together, 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.

The powder to be obtained in this way contains normally at least 10 parts of foreign substances on 100 parts of rubber. Moreover these processes meet serious difficulties by application on a technical scale so that they have not yet 15 come to a technical development.

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 20 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 25 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 30 different processes are known to obtain a granular non-coherent coagulum. This can be performed by adding to the latex large quantities of certain solid substances and coagulating subsequently.

The drawback of these processes is that powders are obtained, which nearly always contain considerable percentages of foreign substances, 35 this giving difficulties for several applications.

4. Processes in which a coagulum is obtained by coagulating latex, to which sodium-nitrite is 40 added (if desired in the presence of substances, which affect the coherence of the coagulum). The crumbly rubber thus obtained is a modified rubber, because the rubber itself has undergone 45 changes. This crumbly rubber has properties which are different from those of other powdery or crumbly rubbers. In many cases these diverging properties will be a handicap when applying 50 these products.

The known processes for preparing a finely divided rubber present therefore serious drawbacks: there are processes which on technical application yield difficulties, which hitherto could 5 not be overcome, while the other processes lead to crumbly or granular products which cannot, or can hardly, be further reduced, or to a fine powder, which however nearly always contains a considerable percentage of foreign substances, or 10 to products wherein the rubber has properties differing greatly from those of the raw rubber.

According to the present invention it is possible to obtain a rubber powder, which contains a very small amount, at the most 5%, of added solid 15 substances and which, if necessary, can further be reduced by grinding. 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 20 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 25 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 to a film and measuring its tensile 30 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 of the 35 coagulum 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 40 reaction is stopped in order to proceed to the separation of the rubber from the liquid.

This separation can be performed in several 45 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 separation is to pour out the liquid in thin layers, to 50 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.

It was found that when fresh latex was used, and if precautions, to be mentioned below, are taken into consideration, the course of the reaction is different and the final state according to the invention is arrived much sooner than in case that old preserved latex was used under the same conditions.

This acceleration of the reaction of fresh latex with respect to that of old preserved latex occurs if the hydrogen ion exponent (pH) of the mixture, the reaction temperature, the vulcanisation accelerator and the concentrations of the reacting substances are chosen in such a way that no decomposition (or only a very small one) of the proteins of the fresh latex takes place.

It is known that in old preserved latex the protein compounds which are by nature present in latex, are no more in the original state, as, in consequence of the alkalinity of the medium and possibly also in consequence of the action of enzymes or bacteria, they have undergone a hydrolysis and a decomposition. The mentioned acceleration of the reaction according to the invention should therefore only be able to take place with old latex, if it were possible to effect the conservation process by adding a non-alkaline reacting substance.

As during the reaction according to the invention alkaline stabilisers have to be added, the reaction conditions should preferably be chosen in such a way that the undesired by-reaction, namely hydrolysis and decomposition of the proteins in consequence of the alkaline medium, does not domineer over the desired reaction.

To obtain this result the pH of the latex mixture should preferably be chosen as low as possible, as far as this does not endanger the stability of the latex mixture, while the reaction temperature should preferably not surpass 90° C and preferably an ultra vulcanisation accelerator is added. Examples of a favorable choice of the reaction conditions are given below.

As it has also appeared that the industrially important properties of the rubber powder to be obtained according to the invention are better if fresh latex is used as starting material, the reaction being carried out while taking into consideration the above mentioned conditions, it is also for this reason that one should start from fresh latex.

The remarkable properties of the rubber powder to be obtained according to the invention, and also the difference in the course of the reaction with fresh latex and old preserved latex must perhaps be explained from the formation of compositions between the protein compounds of the latex and the added reactants. This was shown by the results of comparative tests with fresh and old latex and with latices, wherein the protein compounds had been more or less removed in an artificial way, by application of repeated creaming or repeated centrifuging.

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, also in the absence of free sulphur. This vulcanisation 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 therefore a normal vulcanisation is necessary to give the properties of vulcanised rubber to the rubber obtained according to the invention, the rubber powder cannot be vulcanised in the sense which, until now, was attached to this word; neither can the latex mixture obtained according to the invention, at the moment, the stage has been reached in which the separation of the rubber is started, be called a vulcanised latex.

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 vulcanised by an additional heating to an ebonite mass, which has practically no coherence and therefore is very easily disintegrated to a so-called ebonite powder.

This process means a simplification with respect to the American patent letter 1,849,920 which describes a process for the preparation of ebonite powder by heating latex for 8 to 10 hours under pressure at 141.5° C with 30 to 100 parts of sulphur, if desired in the presence of fillers.

By separation of the rubber from the heated mixture ebonite is obtained, which, if necessary, can be further disintegrated. As it is known, this process cannot be carried out at lower temperature, so that the application is bound to the use of autoclaves.

According to the new process a powder can be obtained by heating the latex below 100° C., after which the vulcanisation to ebonite may be effected by heating to about 140° C., which however not necessarily has to take place in an autoclave.

Therefore the new process can be applied with a much simpler apparatus.

If the rubber powder is formed by coagulation of the pre-treated latex mixture containing an accelerator, 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.....per cent.. | 35.9 |
| Total dry substance content.....do | 38.8 |
| Ammonia content.....grams per litre.. | 1.3 |

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

| | |
|---|---|
| Zinc oxide..... | 1 |
| Sulphur..... | 2 |
| The vulcanisation accelerator "Vulcafor SDC"..... | 1 |

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

| | |
|---------------------------------------|---|
| A 10% ammonia-caseinate solution..... | 2 |
| Water..... | 6 |

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, 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 | Elongation at rupture in percent | Percent combined S calculated on dry rubber |
|--------|---------------------|---------------------------|-----------------------|------------------|----------------------------------|---|
| a..... | Not heated | Normal..... | 7 | 25 | 982 | 0.5 |
| b..... | 1 hour..... | do..... | 5 | 20 | 1090 | 0.6 |
| c..... | 2 hours..... | do..... | 13 | 29 | 833 | 0.7 |
| d..... | 3 hours..... | Coherent but non-elastic. | ----- | 12 | 505 | 1.0 |
| e..... | 4 hours..... | Granular, noncoherent. | ----- | 7 | 223 | 1.4 |
| f..... | 5 hours..... | do..... | ----- | 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 beating 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 | | Stiffness | Tensile strength | Elongation at rupture |
|--------------------|----------|-----------|------------------|-----------------------|
| Temp. | Duration | | | |
| °C. | Minutes | | | Percent |
| 110 | 45 | 36 | 178 | 813 |
| 110 | 60 | 35 | 177 | 802 |
| 110 | 90 | 39 | 179 | 817 |
| 110 | 135 | 32 | 192 | 836 |
| 110 | 180 | 35 | 186 | 831 |
| 150 | 5 | 27 | 213 | 943 |
| 150 | 15 | 15 | 212 | 1068 |
| 150 | 20 | 16 | 206 | 1062 |
| 150 | 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 | Mechanical stiffness while stretching 600% | Properties of the film | |
|-----------|--|------------------------|-----------------------|
| | | Tensile strength | Elongation at rupture |
| 0..... | 2 | 3 | 896 |
| 1..... | 4 | 12 | 984 |
| 2..... | 6 | 20 | 970 |
| 3..... | 8 | 31 | 982 |
| 4..... | 10 | 38 | 971 |
| 5..... | 15 | 41 | 904 |
| 7..... | 20 | 44 | 810 |
| 10..... | 21 | 36 | 723 |
| 14..... | 21 | 29 | 625 |
| 21..... | (1) | | |

¹ Film is brittle.

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. | Properties of the film | | |
|--------------------------|------------------------------|----------------------------|------------------|-----------------------|
| | | Free sulphur in the rubber | Tensile strength | Elongation at rupture |
| Days | | Per cent | (¹) | (²) |
| 28 | ----- | 0.76 | | |
| 28 | 20 | 0.60 | 93 | 640 |
| 29 | 45 | 0.35 | 165 | 615 |
| 30 | 90 | (1) | 162 | 628 |
| 33 | ----- | 0.69 | | |

¹ Not determined.
² Brittle.

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-----per cent-- 40
 Total dry substance content-----do--- 42.9
 Ammonia content-----grams per litre-- 6.1

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

| | Parts |
|-------------------------|-------|
| Zinc oxide----- | 2.0 |
| Sulphur ----- | 40.0 |
| Vulkacit F extra N----- | 0.8 |

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

The mixture of latex and chemicals was heated to 80° C until in a sample, a granular non-coherent coagulum was formed on coagulating with formic acid, which was the case after a heating for three hours. 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 a powder was formed which could be easily ground still further. Thereupon the dry 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 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.

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