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REGENERATING OF VULCANIZED RUBBER

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The present invention relates to improvements in the reclaiming of rubber vulcanizates and comprises a new method of renewing the plastic properties of vulcanized scrap.

Up to the present natural rubber is usually reclaimed by heating the vulcanizates with a highly concentrated caustic soda solution or with a solution of a mineral acid. The use of high temperatures and of softeners is often resorted to in order to produce a uniform and plastic reclaim, such processes being usually accompanied by material decreases in tensile strength. These processes generally require the application of high temperatures of about 180°C, the heating being continued for a prolonged time, say about 5–15 hours. Whereas processes of the character described are practically used for the reclaiming of natural rubber, there is still a lack of suitable reclaiming processes for synthetic rubber-like materials which are obtained by the polymerization of butadiene hydrocarbons or by the copolymerization of such butadienes with other polymerizable substances. The problem of reclaiming such synthetic rubber-like materials is the more grave as the vulcanizates are often built up from a mixture of natural and synthetic rubber and as the presence therein of a preponderant amount of synthetic rubber prevents the products from being reclaimable.

It is the object of the present invention to develop a new process which allows one to effect the reclaiming of rubber at a lower temperature and more quickly than it was possible in accordance with the hitherto known methods. A second object of this invention resides in the developing of auxiliary agents which are suitable for the reclaiming of natural rubber as well as of synthetic rubber-like materials of the character described. Other objects will be apparent from the following description and claims.

It has been found that vulcanized rubber (either natural or synthetic) can be reclaimed by incorporating therewith an aromatic mercaptane, i. e. a compound of the formula R.SH wherein R stands for an aromatic radical, and heating the mixture to a high temperature of for instance about 130 to about 150°C. In accordance with a preferred method of working the heating is effected in an atmosphere containing oxygen at a higher pressure and concentration per cm^3 then it is normally found in the atmosphere. The oxygen may be applied in any desired manner for instance in the form of air or of agents yielding oxygen under the conditions of working. In general, the vulcanizates are treated with the aromatic mercaptanes in the presence of air and steam under pressure. In practice the ground vulcanizates are mixed with the aromatic mercaptane and placed in an autoclave, air being pressed into the same so as to reach a pressure of several atmospheres (say about 2–6), the necessary temperature being generated by causing compressed steam to enter the autoclave so that an increase of pressure of several further atmospheres is effected. The aromatic mercaptanes can be incorporated within the vulcanizates either per se or with the aid of the usual rubber softeners such as "caoutchol".

Examples for suitable reclaiming agents are thiophenols, thiocresols, thionaphthols, thioxylols and thioanthrecenes. In general, these reclaiming agents are employed in an amount of about 1 to about 5% of the vulcanizate. Additional softeners, if any, are likewise employed in an amount of about 5% of the vulcanizate.

The present invention allows one to convert vulcanized natural rubber into a plastic and vulcanizable condition in a much shorter time and at a considerably lower temperature than it was possible in accordance with the hitherto known methods. For giving an example, vulcanized natural rubber can be reclaimed by means of the auxiliary agents of the present invention 4 times as quickly than it would be reclaimed under the same conditions in the absence of aromatic mercaptanes. Synthetic rubber-like materials of the character described can easily be reclaimed in accordance with the present invention, the resulting products showing an excellent plasticity, and, if vulcanized, very often better mechanical properties than vulcanisates of regenerated natural rubber or the original vulcanisates of the synthetic rubber. Therefore, the present invention also allows one to reclaim a vulcanizate which has been built up from a mixture of synthetic rubber and natural rubber even if the former is present therein in a preponderant amount.

Examples for synthetic rubber-like materials which have been employed for the present reclaiming process are the products of the sodium polymerization of butadiene-1.3, furthermore, the products of the emulsion polymerization of butadiene-1.3-hydrocarbons either alone or in admixture with other polymerizable substances such as styrene, acrylic acid nitrile and unsaturated ketones such as vinyl methyl ketone. Furthermore, there may be mentioned the products of the polymerization of chloro-2-butadiene-1.3. As a matter of fact, the present process can be applied to unused rubber scrap as well as to mate-

rials which have undergone a long continued usage.

The present invention is illustrated by the following examples, without being restricted thereto, the parts being by weight:

Example 1

100 parts of a ground vulcanizate of natural rubber is mixed with 3 parts of β-thionaphthol. After a 1–2 hours heating to 130°C the product has been converted into a plastic vulcanizable state. After a several times passing through a refiner one obtains a soft plastic sheet which can be compounded with a fresh rubber mixture. With a similar result the β-thionaphthol can be replaced by an equal amount of m-thiocresol or of m-methoxythiophenol.

In case the heating is effected at an overpressure of air of 2 atmospheres and of additional 4 atmospheres of steam the same result is achieved after a much shorter heating of say about 20 minutes.

Example 2

100 parts of a ground vulcanizate of a synthetic rubber-like material which has been prepared by the emulsion polymerization of 75 parts of butadiene and 25 parts of styrene is mixed with 3 parts of β-thionaphthol. An excellently plastic and vulcanizable product is obtained after a 1½ hours heating to about 130°. The reclaiming process can be performed within about 1 hour in case an overpressure of 3 atmospheres of air and 3 further atmospheres of steam is applied.

Similar results can be obtained by replacing the β-thionaphthol by an equal amount of thioanthracenes or of thiocresols.

Example 3

A ground vulcanizate of a synthetic rubber, which has been prepared by the emulsion polymerization of butadiene and vinyl methyl ketone in the proportion of 1:1, requires a 1 hours heating to 130° in the presence of 3% of m-methoxythiophenol for being converted into a plastic and vulcanizable product. Also in this case the reclaiming can be accelerated by effecting the process in the presence of compressed air and compressed stream.

Example 4

3 parts of β-thionaphthol are incorporated within 100 parts of a product of the conjoint emulsion polymerization of butadiene and acrylic acid nitrile in the proportion of 3:1, 5% of "caoutchol" being employed for securing a better interpenetration of the rubber and the thionaphthol. The mixture is heated for about 1½ hours to 130°C at an overpressure of air of about 2 atmospheres in the presence of 4 further atmospheres of compressed steam. The resulting product shows a good plasticity and exhibits excellent mechanical properties if vulcanized again.

Example 5

Vulcanized scrap containing asbestos fibers can be reclaimed in the following manner: 100 parts of the scrap are mixed with 100 parts of benzine. 5 parts of β-thionaphthol are added thereto, preferably dissolved in benzine and the whole is heated to 150°C for 7–8 hours while constantly agitating and stirring the mixture. The resulting reclaim can be reused for the preparation of vulcanizates. Such vulcanizates containing asbestus fibers are employed in a large scale for the preparation of plates, stuffings and the like.

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