## ALIEN PROPERTY CUSTODIAN

PROCESS OF IMPROVING SYNTHETIC RUBBER AND FACILITATING THE WORKING THEREOF

Carl Zerbe, Hamburg, Johannes Jaenicke and Otto Schweitzer, Frankfurt A. M., Germany; vested in the Alien Property Custodian

No Drawing. Application filed December 23, 1940

This invention relates to a process of improving synthetic rubber and facilitating the working thereof.

The kinds of rubber obtainable by synthesis are produced as a rule by emulsifying in water the monomeric substances to be polymerized or mixtures thereof while adding the usual emuisifying agents and catalysts, and then polymerizing them. The synthetic rubber latex thus produced resembles in many respects natural rubber, is like the latter made into sheets by coaguiation, washing, drying and rolling and constitutes in this form, as smoked sheet or crepe rubber, a raw material for the industry concerned.

These synthetic substances differ, however, 15 under the usual processes. from natural rubber not only in their properties due to the chemical difference of their fundamental substances but also as to the usually considerable cyclization of the molecules forming during polymerization and being per se aiready high-molecular. Due to the difference existing between the chemical composition of their parent substances and that of natural rubber and simultaneous heavy netting through cyclization, these synthetic products show of course a different behavior than the natural product practically at every stage of subsequent working. Particularly when crude mixtures are prepared on the mixers and subsequently molded, synthetic products are extraordinarily hard and require therefore a greater expenditure of energy for these operations than natural rubber. The uniformity of the mixtures found in natural rubber, that is, the good distribution of the ingredients, is also attainable only with difficulty in synthetic products. The measures hitherto proposed to overcome these troubles, such as thermal or chemical decomposition, improve matters to some extent but fail to insure satisfactory working. The addition of softeners of different kinds gives only partial relief, apart from the fact that these softening substances can be added only in slight quantities. Softeners of this class are added during production of the compounds in the mixing arrangements, which still requires extraordinarily great amounts of energy at the beginning of this step when the substances have not yet been distributed in the polymerization product.

As aids in working synthetic rubber, the extraction residues accruing in the refining of different mineral oil fractions with selective solvents, the distillates thereof and also the corresponding hydrocarbon mixtures, partly unsatu- 55 rials of synthetic rubber already during produc-

rated and partly soluble in concentrated sulfuric acid, obtainable from the acid tars developed during refining of crude oils with concentrated sulfuric acid by neutralization or hydrolysis or extraction and, possibly, distillation have given particular satisfaction. Suitable for this purpose are also the natural unchanged crude oils, as miri oils and similar hydrocarbon mixtures, which are especially rich in substances tending to 10 resinify.

It has also been proposed to add these substances to the latices of the various sorts of synthetic rubber so as to provide a denser structure for the objects directly produced from latex

It has now been found, according to the invention, that by the joint coagulation of mixtures of synthetic rubber latices, or of dispersions of synthetic rubber derivatives, and of the emuisions of softening substances and by washing, drying and rolling products are obtained that are adapted to a particularly high degree to serve as starting materials for the rubber industry. Such joint coagula representing intermediate products may be produced for instance by making use of the possibly previously concentrated aqueous dispersions of the polymerization products of butadiene, its homologues and derivatives, or of the mixed polymerization products thereof with vinyi compounds, as styrene or acrylonitrile, of similar ethylene and vinyl compounds and also of the conversion products of allphatic dihalogen compounds and alkali polysulfides. The polymerization products of methyl-butadiene, or isoprene, which must be considered a homologue of butadiene, are accordingly also included in this class.

In further accordance with the invention, the additional substances to be used comprise the extracts or distillates obtainable by refining mineral oils with selective solvents, as furfurole, suifur dioxide, suifur dioxide in mixture with organic solvents like benzene, etc., or from the acid tars produced in refining with concentrated suifuric acid either after neutralization with suitable agents or by hydrolysis with water, water vapor, etc. These substances represent mixtures of hydrocarbons partly unsaturated and partly soluble in concentrated sulfuric acid. Suitable for the process are also certain crude oils occurring in nature, such as miri oils, which are rich in substances tending to resinify.

The common coagula can be prepared also by adding the softening agents to the basic matetion, that is, before the completion of polymerization at the earliest, whereupon these mixtures are completely polymerized, coagulated and subsequently worked as usual. A substance may therefore be added in the form of aqueous dispersions or emulsified already in the emulsion of the polymerization products, in other words, it may be added at any time between actual polymerization and the production of the coagula. The quantities of the additional substances according 10 to the invention may very within wide limits.

to the invention may vary within wide limits.

The application of the process according to the invention insures such fine distribution of the softening additions in synthetic rubber that

working of the latter on the mixers is surprisingly facilitated even at the beginning of the mixing operation. If softening to a particularly high degree is desired, the mixtures of substances thus produced may be decomposed by known methods prior to being treated in the mixing arrangements. It is even possible to subject the mixtures when still in latex form to a heat or chemical treatment, for instance with the aid of oxidizing agents, and then to continue further working of the mixtures formed.

CARL ZERBE, JOHANNES JAENICKE, OTTO SCHWEITZER,