

# ALIEN PROPERTY CUSTODIAN

## PRODUCTION OF SYNTHETIC RUBBER

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This invention relates to a process of producing synthetic rubber.

For quite some time, products resembling natural rubber as to properties and applicability have been prepared from monomeric butadiene hydrocarbons and their derivatives. Of these substances the mixed polymerization product of butadiene and styrene or acrylonitrile has given particular satisfaction during the last years, though these substances differ from natural rubber not only in the properties due to the chemical difference of their fundamental substances but also in the usually considerable cyclization of the molecules forming during polymerization and being per se already high-molecular. During subsequent working both causes bring about a behavior of these polymerization products which differs from that of natural rubber. The masses are comparatively hard, so that it is difficult, with the usual mixing arrangements, to prepare therefrom homogeneous mixtures with the usual additions, as fillers and vulcanizing agents. The finished mixtures are, as a rule, stiff and can be molded only with difficulty.

To facilitate the working of these products it was necessary to resort to measures, including for instance different decomposition methods, absolutely unusual in working natural rubber. The use of softeners and similar expedients, known already from the working of natural rubber, has been accepted to an increasing extent also in working the new polymerization and mixed polymerization products. A number of aids specifically effective in working these products was discovered also. Special mention in this respect deserve hydrocarbon mixtures partly unsaturated and partly soluble in concentrated sulfuric acid, reactive and possibly distilled at reduced or atmospheric pressure, which accrue, when all sorts of mineral oil fractions are refined with selective solvents or which are obtainable from the acid resins developed during refining of the oils with concentrated sulfuric acid by neutralization or hydrolysis or extraction or, possibly, distillation. These substances are added during production of synthetic rubber mixtures in the mixing arrangements at an extraordinarily great expenditure of energy at the beginning of this procedure when these substances are not yet distributed in the polymerization product.

It has now been found, according to the invention, that these substances obtained in refining mineral oils may be added in dissolved or dispersed form to the substances to be polymerized either prior to the beginning or at least the completion of the polymerization and that the additions are then ideally distributed among the macromolecules forming during polymerization. The hydrocarbon mixtures referred to above are thus added to the monomeric compounds or mixtures thereof serving for forming

the polymerization products, and this should be done at an early stage of polymerization at the very latest. The amounts of the additions may be adapted within wide limits to the requisite reaction conditions and the expected properties of the final product. It might easily happen in this connection that, apart from mere physical intercalation, the reactive portions of the additions according to the invention are more or less chemically combined with the macromolecules forming, possibly through residual affinities. A particularly favorable distribution is further insured by the fact that the low-molecular portions may serve as solvents for the hydrocarbon mixtures according to the invention.

The process may be applied to the production of the polymerization products of butadiene, its homologues and derivatives, or of the mixed polymerization products thereof with vinyl compounds, as styrene or acrylonitrile, or of the polymerization products of other monomeric ethylene and vinyl compounds. The homologues of butadiene include also methyl-butadiene, or isoprene, which supplies the true synthetic rubber.

To attain the effects contemplated by the invention the extracts or distillates obtainable by refining mineral oils with selective solvents like furfurole sulfur dioxide, sulfur dioxide in mixture with organic solvents like benzene, etc., or from the acid tars produced by refining the oils with concentrated sulfuric acid after neutralization with suitable agents, or by hydrolysis with water, water vapor, etc., may be employed. These substances represent mixtures of hydrocarbons partly unsaturated and partly soluble in concentrated sulfuric acid. Furthermore, certain mineral oils occurring in nature, such as the miri oils, which are rich in substances showing a tendency to resinify, are also adapted for the process.

A particular advantage afforded by the process is that the softening additions are ideally distributed already in the synthetic rubber before the latter is worked on the rollers. The mixture of substances thus produced is therefore plastic enough for the first stage in the rolling operation. It is further highly advantageous that the heat liberated during polymerization is absorbed also by the substances added according to the invention. Owing to the loosening up of the arrangement of the particles to be polymerized, a welcome damping of the frequently quite stormy course of the reaction is effected.

The mixtures may be polymerized undiluted or in the presence of solvents or in emulsion. Depending on the process applied, the usual catalysts, as metallic sodium, tin tetrachloride, peroxides, etc. may be used.

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