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PRECIPITATION OF EMULSION POLYMERIZATES

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The present invention relates to improvements in the emulsion polymerization of unsaturated compounds and in particular in the preparation of synthetic rubber-like materials.

The best hitherto known synthetic rubber-like materials are those prepared by the emulsion polymerization of butadiene hydrocarbons and particularly of mixtures of butadiene hydrocarbons and compounds containing an activated vinyl group, such as styrene, acrylic acid esters, acrylic acid nitril, the corresponding methacrylic acid derivatives or fumaric acid esters. The emulsion polymerization can be performed in an alkaline, neutral or acid medium. Suitable emulsifiers for the working in an alkaline medium are, for instance, alkylnaphthalene sulfonic acids or soap forming fatty acids. On the other hand, the working in an acid medium requires the application of so-called "cationactive" emulsifiers such as mineral acid salts of higher fatty amines or of esters prepared from higher fatty acids and aminoalcohols. As a result of the emulsion process the polymeric products are obtained in form of a "latex" closely resembling that of natural rubber. Depending on the nature of the emulsifying agent the solids are precipitated from the emulsion in various ways. Thus, neutral reacting electrolytes can be employed in the case of a neutral or nearly neutral medium. Acids such as acetic acid have proved to be suitable for the precipitating of the solids from a strongly alkaline medium, the best results having been obtained by first precipitating such emulsions by means of neutral reacting water soluble salts such as sodium chloride and then rendering irreversible by the addition of acids the reversible precipitate thus obtained. From acid emulsions the solids can be precipitated for instance by means of alkaline reacting agents such as sodium carbonate or by means of alkali bisulfites and the like. The best suitable precipitating agents for the alkaline, neutral or acid emulsions, as the case may be, are partly described in literature and can in each case be easily determined by simple tests. Nevertheless the working up of such emulsions is connected with considerable difficulties chief among which is to be seen in the fact that the solids are often liable to stick together thus forming a strongly coherent cake the tough nature of which represents a serious obstacle for washing, purifying and drying operations. On the other hand, in the dry state the plasticity and softness of such polymerizates is inferior to that of natural rubber so that some difficulties are encountered in the uniting of the solids into a sheet of the kind made use of in the rubber industry.

Similar difficulties are encountered in the emulsion polymerization of such unsaturated compounds as yield other products than rubber-like materials, though only part of such products is liable to stick together after the precipitation. On the other hand, there exists in every case the problem of effecting the precipitation in such a manner as to allow one completely to remove any impurities from the solids by washing operations. The removal of such impurities represents a serious problem in the preparation of such materials as it is evident from the fact that they are often employed for the preparation of transparent materials such as safety glass or electrical purposes.

It is the object of the present invention to do away with these difficulties and to develop a new process which allows one to precipitate the solids from such emulsions in a finely divided state in which they are not liable to stick together and can be led off through pipe lines together with the aqueous medium without inducing the danger of obstructions. Another object of our invention resides in the conducting of the precipitation process in such a manner that the solids can be easily purified by washing out. Still another object of our invention resides in the modifying of the individual precipitated particles in such a manner that they become sticky in any desired stage of the working up operations. In accordance with still another feature of this invention the becoming sticky is conducted in such a manner that the individual particles of the solids can be assembled into a coherent dry sheet without preventing the previous washing out and purifying operations. Still another object of our invention resides in the performing of such steps in a continuous manner, i. e. in a form which is particularly fit for the working in a technical scale. Other objects will be apparent from the following description.

Our invention in its simplest form comprises the performing of the precipitating step under such conditions that every unit of the emulsion is contacted with at least that amount of the precipitating agent which is necessary for effecting complete precipitation thereof, and in particular with an excess over the necessary amount. This can be accomplished for instance by pouring or dropping the emulsion slowly into or onto a solution of excess precipitating agent while stirring. In accordance with a preferred form of our invention a streaming emulsion of the character described is united with a streaming aqueous solution of excess precipitating agent. This procedure has proved to be very suitable for preventing any unit of the emulsion from being contacted with an insufficient amount of the precipitating agent, and at the same time allows one to conduct the precipitating step in a continuous manner. Both methods of working result in the formation of a finely divided precipitate which is not liable to stick together

and which is capable of being led off through gutters, channels, pipe line, and the like together with the liquid medium without giving rise to any agglomerations and obstructions. It is evident, that such properties of the precipitates which are obtained in accordance with our invention are doing a good share towards conducting the working up operations in a continuous manner.

Another feature of our invention resides in the discovery that the finely divided non-sticky particles thus obtained can be agglomerated by very simple manipulations. In the case of synthetic rubber-like materials of the character described this effect is best accomplished for instance by mixing the aqueous medium containing the solids with a multifold quantity of water. As such agglomeration is connected with and caused by an increase of the sticky character of the precipitate such operation must be applied at such a stage of the working up operations that no obstructions can occur any longer. In the case of a continuous precipitating process making use of a pipe line for the leading off of the precipitate together with the aqueous medium the addition of water is effected for instance shortly prior to or after the precipitate's leaving the pipe line. In consequence of the said agglomeration of the synthetic rubber the particles have assumed such a size that they are capable of being freed from the water by filtration. Therefore, our invention furthermore contemplates the passing of the agglomerated particles onto a filter for washing and purifying purposes. In accordance with a preferred form of working we are taking a continuously working filter such as an endless band filter or a revolving filter. In this manner the whole working up process beginning with the precipitating and ending with the drying can be performed in a continuous manner. An outstanding feature of our invention is to be seen in the fact that the agglomerated particles can be brought to a high degree of purity by irrigating the same with water while resting on the filter, and that on becoming dry they are liable to stick together thus forming a coherent rubber sheet of the type desired by the rubber factories. The removal of the water can be accelerated by mechanical means for instance by squeezing rollers or by the application of reduced pressure. It is preferred, however, to reduce the water content of the synthetic rubber-like material while being in contact with the filter not beyond the limit of about 50% in order to avoid undesirable obstructions of the mashes. The remaining water is best removed by leading the sheets through heating chambers it being to be understood that also these operations can be performed in a continuous manner.

The foregoing paragraph was concerned with the agglomerating purifying and uniting into a coherent sheet of synthetic rubber-like materials, it being to be understood that such operations are not restricted to rubber-like materials but can be applied also to such emulsion polymerizates as are suitable for other purposes than as substitute for rubber, always provided, however, that they show a sufficient liability to stick together. Such polymerizates are for instance those prepared from acrylic acid esters and vinyl esters or from mixtures of the same.

In the case of those emulsion polymerizates the precipitated particles of which are not liable to stick together, such products being for instance polystyrol or polyvinylchloride, the precipitating process as described above allows one to free such precipitates from the last traces of any impurities though the uniting into a coherent sheet is impossible in those situations. The finely divided state of the precipitates obtained in accordance with the present invention prevents or at least diminishes the danger of impurities being occluded within the solids so as to be not removable by contact with water. On the other hand, such finely divided precipitates are also capable of being agglomerated so as to be converted into a state in which they can be washed out and separated from the aqueous medium by mechanical means, for instance, on the filter or in a centrifuge. Depending on the nature of the material the agglomerating can be performed either by the addition of water as it is more fully described above for the rubber-like materials or for instance by the application of a higher temperature. The necessary rise of temperature can be effected for instance by blowing in steam.

It has been disclosed in the foregoing paragraphs in which manner our new process can be performed. In the following we are giving some details regarding the necessary amount of precipitating agents for various emulsions and various precipitating agents it being to be understood that in other cases the nature and the requisite amount of the coagulants can be easily determined by tests and that the following figures can be employed for a discontinuous as well as for a continuous working. In the following table there are given the parts by volume of salt and/or acid solutions which have been found to be suitable for effecting complete precipitation of 50 parts by volume of a 30 per cent emulsion of various synthetic rubber-like polymerizates, the concentration of the salt solutions being in each case 8 per cent and of the acid solutions 1 per cent unless otherwise stated, and also the parts of water which are used for the agglomerating:

(1) Mixed polymerizate of butadiene and styrol in the presence of alkylnaphthalene sulfonic acids and fatty acid salts as emulsifiers, the aqueous medium showing an alkaline reaction.	90 parts of a sodium chloride solution and then 30 parts of an acetic acid solution and then 200 to 300 parts of water.
(2) Mixed polymerizate as described sub 1 with the exception that the butadiene and the styrene are contained therein in the proportion of about 5.5 to 4.5.	(a) 120 parts of a sodium chloride solution and then 30 parts of an acetic acid solution. (b) 10 parts of a calcium chloride solution and then 30 parts of an acetic acid solution. (c) 20 parts of a magnesium chloride and then 30 parts of an acetic acid solution. (d) 40 parts of a potassium chloride and then 30 parts of an acetic acid solution.
(3) A nearly neutral emulsion of a mixed polymerizate of butadiene and acrylic acid nitrile in the proportion of 3:1, the emulsifyer being sodium alkylnaphthalene sulfonate.	(a) 200 parts of a sodium acetate solution. (b) 20 parts of a calcium chloride solution. (c) 40 parts of an aluminum acetate solution and then 30 parts of an acetic acid solution.
(4) An emulsion as described sub 3, the butadiene and the acrylic acid nitrile being in the proportion of 3:2.	(a) 20 parts of a calcium chloride solution. (b) 20 parts of a magnesium chloride solution.
(5) An acid emulsion of the polymerizate described sub 1 in the presence of dodecylamine chlorohydrate.	50 parts of a 6 per cent sodium hydrosulfite solution.

It is to be understood that in each case the agglomerating can be effected by adding 200 parts of water to the precipitated emulsion.

As to styrene and similar starting materials for the preparation of materials other than those of a rubber-like character, the emulsion polymerization of such products can be performed for instance in the presence of sodium oleate, i.e. in an alkaline medium. In these cases formic acid can

be employed for the precipitating step. The amount of the same must be so chosen that the emulsion is rendered at least neutral or slightly acid. Thereupon we prefer to add ammonia to the precipitate so as to render it alkaline again. This step is taken in order to dissolve the oleic acid which has been precipitated together with the polystyrene, it being to be understood that no re-emulsification occurs thereby. The agglomeration can be performed by blowing in steam.

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