PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Process for the Preparation of Rubber Hydrohalide Dispersions

We, RUBBER-STICHTING, a Foundation incorporated under the Dutch Laws, of Julianalaan 134, Delft, Holland, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to a process for the preparation of rubber hydrohalide dispersions in which hydrogen halide, particularly hydrogen chloride, reacts with latex. From this latex derivative the solid product can be obtained by evaporation, coagulation or other known methods.

Hitherto it has only been proposed to make rubber hydrohalide, particularly rubber hydrochloride, in solid or in dissolved form. This solid product was obtained by subjecting crepe rubber or rubber sheet milled to thin sheets to the action of hydrogen chloride (HCl).

According to other known methods HCl gas is passed through a rubber solution whereby rubber hydrochloride is formed in the solution. The reaction can be brought about at various temperatures, but preferably at a very low temperature. From the solution above mentioned the reaction product is obtained by precipitation or by evaporation of the solvent.

Working with solutions, however, has the drawback that these solutions are not very concentrated so that the yield per unit volume of the reaction space is small; moreover recovery of a solvent makes the process expensive. Working at such a low temperature moreover makes the process costly.

When introducing HCl gas into fresh or ammoniated latex, coagulation takes place at the iso-electric point, *p*H value 4.8 According to H. C. Baker, Proc. Rubber Techn. Conf. London 1938, 209 rubber does not react with HCl when large quantities of water are present.

We have found, however, that it is possible to prepare in latex a rubber hydrochloride in dispersed state. For this purpose it is however, necessary to subject the latex to a pretreatment, by which the latex is stablized in the greater part of the acid *p*H range.

When introducing HCl gas into such a latex a dispersion of rubber hydrochloride is formed. That dispersion gives, also microscopically, the impression to be a dispersion of unaltered latex. On chemical examination it appears, however, that indeed a rubber hydrochloride dispersion has been formed. From this dispersion a solid product can be recovered.

For the preparation of a latex stable in an acid medium various methods are known.

A known method is e.g. to pour the latex into an excess of acid of a certain strength.

In this manner the so-called second liquid stage is reached with a *p*H value from 3.5 to 2. This latex is positively charged. From a practical point of view this method is not very suitable because the latex is very unstable and can only be obtained in low concentrations. By the addition of casein, saponin, hæmoglobin and the like products this latex can, however, be made considerably more stable. A second method which is more suitable for the process according to the invention is the addition to the latex of cation soaps, such as the bromide or chloride of the N-cetylpyridinium ion (sold under the Registered Trade Mark "Fixanol"), the alkali salts of methyl oleylamide ethyl sulphate (sold under the Registered Trade Mark "Igepon T"), or the acetate, hydrochloride or methosulphate of (diallylaminoethyl)-fatty acid amide (sold under the Registered Trade Mark "Sapamin"). In this manner a stable latex with higher concentration can be obtained. Whereas, however, with the application of "Fixanol" fresh latex or not too old latex can immediately be treated with "Fixanol", it is desirable

[*Price* 2/-]

when using old latex or e.g. latex sensibilized by heating, to remove the decomposition products of the proteins before the treatment with "Fixanol" in order to prevent any partial coagulation.

As suitable is a latex to which is added a non-ionogenic emulsifying agent, such as dodecylphenolpolyglycolether (sold under the Registered Trade Mark "Igepal" or the product sold under the Trade Mark "Emulphor". Thus a latex is obtained which is stable with respect to acids in a larger *p*H range.

If the original latex is natural latex it may be fresh or preserved with ammonia. In the latter case the ammonia may be removed before pretreating the latex (charge-reversal). This may be brought about by passing air, or better still an inert gas such as nitrogen, through the latex or by adding a certain quantity of formaldehyde, by which the ammonia is converted into hexamethyleuetetramine. The presence of this substance in the final product may be advantageous in respect of stability to light.

The natural latex can moreover be first concentrated before the charge of the rubber particles is reversed.

Also vulcanized latex, white or yellow fraction (obtained according to the co-pending Application No. 7844/41 (Serial No. 594,938)) or skim as obtained by creaming, centrifugal action or coagulation serum can be started from. Also deproteinized latex can be used as starting material. Deproteinized latex can e.g. be obtained by boiling with alkaline hydroxides followed by dialysis, by decomposition of proteins with e.g. bacteria, by adsorption displacement and by other methods or by a combination of various purification methods.

The method of adsorption displacement offers the possibilty of adsorbing to the particles, at the same time as the purification, a substance having the property of stablizing latex in acid medium. A pretreatment for the purpose of making the latex acid resistant can then be omitted. If e.g. "Emulphor" is used as protein displacing substance a purified acid resistant latex is immediately obtained.

By " acid resistant" latex is meant a latex which does not coagulate by the addition of acid but in which possibly an agglomeration can occur.

Besides natural latex the initial material may also be synthetic latices or artificial dispersions of rubber.

If it is desired to prepare rubber hydrochloride from synthetic latex it is preferable to start from a latex which according to the emulsion-polymerisation process is immediately obtained as an acid-resistant latex because the polymerisation is obtained in the presence of cation soaps or of a non-ionogenic emulsifying agent. Consequently synthetic latices need not be pretreated before the hydrochlorination when they have been polymerized in such a manner that they are stable in acid medium. Examples of synthetic latices reacting completely or partially with HCl are e.g. polyisoprene, polydimethylbutadiene, polymethylpentadiene or the co-polymer of isoprene and isobutylene.

In artificial dispersions an acid-resistant dispersion can already be made during the preparation by dipersing the rubber in a solution of cation soaps.

According to the invention HCl is caused to react on a latex, stable with regard to acid, obtained by one of the above methods, by passing HCl gas into the latex, preferably while stirring. In the beginning of the process agglomeration usually occurs, in the further course of the reaction a finely divided dispersion is again formed which appears to consist of homogeneous rubber hydrochloride.

Thus the formation of the agglomerate does not prevent the formation of the rubber hydrochloride. The phenomenon depends on the origin, the concentration, the purity and the pretreatment of the latex as well as on the reaction temperature, the velocity of the introduction of HCl gas and of reagents which, if desired, may be present, e.g. acids, creaming agents.

The occurrence of the agglomerate may have certain advantages for the technical preparation because a kind of concentrated latex can intermediately be formed.

When introducing HCl gas into the latex first a saturation of the water with the gas takes place. It is consequently cheaper to start from dispersions with as little water as possible.

Acidification can in principle also take place with another inorganic or organic acid, but this does not give an advantage, as it is possible to regenerate the HCl from the serum, after removal of the rubber hydrochloride.

The HCl only enters into reaction with the rubber-globules or -flocs if the water is completely saturated with HCl; this point is reached after an introduction period which depends on the rate of introduction of the HCl gas. The rate of the HCl addition to the rubber is dependent on the pressure and temperature. In this manner it is possible to control the starting point as well as the velocity of the reaction within very wide limits by these three factors.

During the reaction the above factors can also be varied. In this manner a cer-

tain degree of hydrochlorination can be reached.

The mixture becomes highly liquid during the reaction and again assumes the form of an emulsion. In this emulsion the rubber hydrochloride particles are dispersed in the same manner as is the case with the rubber particles in latex. By the rubber hydrochloride being obtained in the form of an emulsion all kinds of purification methods known for latex can easily be applied. The solid rubber hydrochloride can be recovered from that dispersion by precipitation, flocculation, sedimentation, if desired combined with centrifugal action or by means of other methods. It is advantageous that the rubber hydrochloride thus obtained is recovered in very finely divided form. The precipitation can e.g. be effected by the addition of alcohol, acetone, dioxane, and the like.

As the specific gravity of the latex and thereby the tendency of the particles to be creamed, or to settle varies corresponding to the HCl content, one has herein a simple test to follow the reaction and to prepare a rubber hydrochloride dispersion with a predetermined chlorine content. In this manner a product with a desired chlorine content can be easily prepared.

When the hydrochlorination of the latex is carried to completion a rubber hydrochloride is obtained with a higher Cl content than that prepared according to the processes hitherto known. This higher Cl content is probably obtained because no oxidation of the rubber has taken place during plasticizing. The products prepared according to the process contain 98—99% of the theoretical quantity of chlorine, whereas with the known process the same amounts to 85—95%.

The molecular weight of the product of the invention is higher than that of the known products which is advantageous for the manufacture of films and fibres.

Instead of reacting HCl gas with a rubber dispersion it has also been found to be possible to react HCl gas with a floculate. Besides HCl also other hydrogenhalides, such as HBr and HI can react with latex.

It has been found to be possible to modify the properties of the rubber hydrohalide dispersions by the addition to the starting latex or to the final product of softening agents, plasticizing agents, stabilizers against acid formation or against ageing (butylstearate, diphenylguanidine, hexamethylenetetramine), active and inactive fillers, vulcanizing agents, oxides such as MgO, CaO, PbO combined or not combined with vulcanizing agents, and pigments.

It is known that vulcanization of rubber hydrochloride can take place with S, sulphides, S_2Cl_2, $ClSO_3K$, SO_2Cl_2.

The rubber hydrochloride dispersion can, provided that the aqueous medium does not give difficulties, also be vulcanized with these substances. These substances can be added to the starting latex as well as to the rubber hydrocloride dispersion.

The following Examples will further illustrate the invention but the invention is not limited to these Examples.

EXAMPLE 1.

For the removal of ammonia, nitrogen is passed for some hours through a 40% latex preserved with ammonia. Thereupon the rubber content of the latex is reduced to 10%, and 50 ccm. hereof 6 ccm. of a 5% "Fixanol" solution are added. Subsequently under cooling, HCl is introduced into this mixture until saturation, whereupon HCl gas is slowly passed through the mixture for three days.

After precipitation with alcohol, and washing, the chlorine content of the final product amounts to 33.5% Cl (This is 99% of the theoretical value).

EXAMPLE 2.

Nitrogen is passed through preserved creamed latex (60%) until the ammonia present therein has been removed for the greater part. Thereupon 17.5 ccm. of a 10% "Fixanol" solution is added to 50 ccm. of 60% latex. By this addition the latex assumes a pulpy consistency. With good stirring HCl is introduced under cooling. After leading in HCl for one hour the mixture is saturated with HCl and after approximately 1½ hours the latex has become highly liquid. After slowly passing HCl through for three days the rubber hydrochloride is isolated. Chlorine content 28.9%.

EXAMPLE 3.

10 ccm. of a 5% "Igepal" solution and 40 ccm. of 4N HCl were added to 15 ccm. of a 40% latex. HCl gas was passed through for 4 days. During the first 3 hours the reaction mixture was cooled. At the end of the reaction the product was isolated by precipitation with alcohol and dried. After having been dissolved in benzene and again precipitated with alcohol the chlorine content after drying amounted to 33%.

The rubber hydrochloride prepared according to the invention can be used for the same purposes for which rubber hydrochloride prepared in other ways is used, e.g. for films, coatings, as impregnating agent, adhesive and the like.

The products according to the invention are strongly crystallized and not soluble in all solvents. The product is e.g. insoluble in carbon tetrachloride but soluble in hot toluene.

It is possible to manufacture articles from the rubber HCl emulsion in the same way as from rubber latex, e.g. by dipping, moulding or impregnating.

Finally the rubber hydrochloride latex can serve as a starting material for the preparation of new derivatives, which derivatives if desired, can also be obtained again in the form of latex.

Example 4.

33 ccm. of a latex with a rubber content of 40% were stabilized with 100 ccm. of a 1% " Fixanol " solution by which a 10% acid-resistant latex was obtained. This latex was saturated at 0° C. with HCl in quantities of 25 ccm., brought into Carius tubes and heated. The result of the heating at various temperatures and during various periods is indicated in the following table.

Heating at 60° C.

Period of heating in hours	1	4	5.5	22
% Cl by weight	18	29.3	29.2	33

Heating at 90° C.

Period of heating	10 min.	20 min.	30 min.	60 min.	6 hours	22.5 hours
% Cl by weight	21.8	28.0	30.3	33.5	33.5	33.5

Also with diluted latex, so-called skim, good results can be obtained as appears from the following Example 5.

Example 5.

Into 50 ccm. of skim with 5% of rubber to which 5 ccm. of a 5% " Fixanol " solution were added hydrochloric acid gas was passed through under cooling and after saturation hydrochloric acid was slowly passed through for further 40 hours. After termination of the reaction the product was coagulated with alcohol, washed and dried. The chlorine content of the product was 33.2%.

Besides hydrochloric acid also other halide acids can give addition products with rubber. With HBr a rubber hydrobromide was obtained in the same way.

Example 6.

To 100 ccm. of latex with 40% of rubber 2.4 ccm. of a 5% "Fixanol" solution were added after removal of the ammonia from the latex and to the latex stabilized in this manner 10 ccm. of a 25% HBr solution were added. Thereupon HBr is passed during 5 hours under cooling with ice-water whereupon the reaction mixture is allowed to stand over night. After coagulation with alcohol, filtration, washing and drying a white powder was obtained containing 51.8% of Br, that is 95.5% of the theoretical quantity.

Example 7.

20 ccm. of latex (40%) from which the greater part of the ammmonia has been removed are stabilized with 100 ccm. of a 5% " Fixanol " solution. Thereupon 50 ccm. of water are added, and the latex thus obtained is saturated with hydrochloric acid gas at −20° C.

Portions of 25 ccm. are brought into Carius tubes and the tubes are sealed.

During various times the tubes are left to themselves at +20° C. By this treatment the reaction mixture comes under a pressure between 3 and 5 atmospheres.

Result:—

Time	45 min.	75 min.	130 min.	150 min.	4.5 hours
% Cl by weight	8.5	14.6	24.3	28.8	32.1

Example 8.

For the preparation of rubber hydrochloride with a predetermined chlorine content the reaction is carried out relatively slowly. By introducing HCl into e.g. 30% acid-resistant latex at room temperature, at normal pressure and under stirring the conditions can thus be chosen that the chlorine content in the reaction product increases by 1% Cl per hour of reaction period.

By the execution of such an experiment HCl was passed through during 24 hours after the latex had been saturated with hydrochloric acid. The isolated reaction product contained 23.6% of Cl by weight.

Example 9.

In an autoclave of acid-resistant material of 15 litres capacity 10 litres of a 50% acid-resistant latex, saturated with HCl, were brought. The latex was heated at 90° C. and the pressure was simultaneously brought to 25 at. using a bomb containing HCl under pressure.

25 minutes after the reaction mixture had been brought at 90°C. the reaction product was isolated and purified.

Yield: 7.25 kg. of rubber hydrochloride with 33% Cl by weight.

EXAMPLE 10.

0.6 g. of "Emulphor O" in solid form was added to 55 ccm. of 60% latex (creamed or centrifuged) (i.e. 2% of emulsifying agent "Emulphur O" calculated on DRC of the latex). With intensive stirring HCl gas is introduced. After passing HCl slowly through the dispersion during five days the rubber hydrochloride is isolated. Chlorine content 30.1%.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. Process for the preparation of rubber hydrohalide dispersions characterized in that a hydrogen halide is made to react with acid-resistant aqeuous rubber dispersions as herein defined, particularly with latex.

2. Process according to Claim 1 characterized in that hydrochloric acid gas is made to react with a rubber latex which has been deproteinized and rendered acid-resistant by means of adsorption displacement, particularly by addition of a non-iongenic emulsifying agent to the the latex.

3. Process according to Claim 1 or 2 characterized in that the gaseous acids are made to react with the rubber dispersions under increased pressure and, if desired, at increased temperature.

4. Process for the preparation of a solid product from the addition products obtained by a process according to any of the preceding claims be evaporation, precipitation, flocculation, sedimentation or the like, if desired, preceded or combined with known purification methods.

5. Articles, vulcanized or not, from rubber hydrohalide prepared from the addition products obtained with the aid of the process of any of the preceding claims.

6. Articles, vulcanized or not, from rubber hydrohalide prepared with the aid of the dipping method from dispersions obtained according to the process of any of the Claims 1 to 3.

7. As a new composition of matter an aqueous dispersion of rubber hydrohalide when prepared or produced by the methods or processes of manufacture particularly described and ascertained.

8. The process of preparing rubber hydrohalides substantially as described in any of the foregoing Examples.

9. Rubber hydrohalides when obtained in accordance with any of Claims 1 to 4 or 8.

Dated this 23rd day of October, 1947.

J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields,
London, W.C.2,
Chartered Patent Agents.

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5. Articles, vulcanized or not, from rubber hydrohalide prepared from the addition products obtained with the aid of the process of any of the preceding claims.

6. Articles, vulcanized or not, from rubber hydrohalide prepared with the aid of the dipping method from dispersions obtained according to the process of any of the Claims 1 to 3.

7. As a new composition of matter an aqueous dispersion of rubber hydrohalide when prepared or produced by the methods or processes of manufacture particularly described and ascertained.

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