

NOTE ON THE PRODUCT OF A REACTION BETWEEN AQUA REGIA AND LATEX

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Summary

Details are given of a method by which latex may be caused to react with a mixture of nitric and hydrochloric acids to form a free-flowing powder. Some of the chemical and physical properties of the product are described.

Arising from experiments to repeat on fresh latex the halogenation experiments made by H. C. Baker (1938) on ammoniated latex, the sodium chlorate and hydrochloric acid reagents were replaced by *aqua regia*. After numerous unsuccessful trials with different stabilisers and combinations of mixed acids a method was evolved which produces a product in the form of a fine free-flowing powder. R. L. Sibley (1941) stated in a recent lecture that a wide variety of products could be obtained from rubber by reaction with increasing proportions of *aqua regia* and this note gives the details of a method of producing an interesting product by the action of *aqua regia* upon rubber in the form of fresh latex.

Method

In a water bath arranged to admit a flow of cold water, set up a six-litre bolt-head flask fitted with a mechanical stirrer and a dropping funnel. Place 100 ml. of fresh latex (35-40 per cent dry-rubber-content) in the flask and stir in 24 grams of "Lissapoi A" paste mixed with 200 ml. of water, followed by 600 ml. of concentrated hydrochloric acid. The temperature of the water surrounding the flask should be about 50°C. initially and when the contents reach this temperature 150 ml. of concentrated nitric acid are run rapidly from the dropping funnel into the latex mixture with constant stirring. The reaction gradually gathers momentum and the water in the bath heats up rapidly if not changed, but by admitting a steady stream of cold water to the bath the reaction can be controlled and the temperature of the reactants kept down to about 80°C. Copious fumes of nitrogen peroxide are at first evolved but when these have subsided the water is run out of the bath and the reaction mixture allowed to stand overnight.

The product is a fine yellowish-brown powder which settles readily and is easily washed by decantation, finally filtered on a Buchner funnel and dried in a vacuum desiccator.

OBSERVATIONS MADE DURING THE DEVELOPMENT OF THE METHOD

If the above procedure is used with the exception that the temperature of the reacting mixture is kept below 10°C. by the use of ice, the product is not homogeneous—part is rubbery and the remainder has the texture of brown factice. If the initial temperature is not more than 25°C., the reaction temperature does not rise above 30°C. and a brown coagulum forms. The addition of the nitric acid before the hydrochloric acid is not as effective as the order recommended.

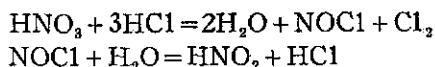
It was thought that the reaction might be more readily controlled if the latex was at a sufficiently high temperature to cause instantaneous reaction, and experiments were made accordingly.

Latex in the presence of "Lissapol A" and hydrochloric acid coagulated when the temperature approached 100°C.; when the acid was omitted a thick paste formed at that temperature. Latex and stabiliser without acid remained liquid at 80°C. but hard lumps were formed when the previously mixed hydrochloric and nitric acids were added. At 70°C. in the presence of hydrochloric acid and stabiliser the latex remained fluid but on addition of nitric acid coagulation occurred. Commencing with the latex and acid mixture at 60°C. all the nitric acid was added before flocculation occurred but lumps were formed when the vigorous reaction set in. However, it was found that these lumps readily broke down to a fine powder on a Buchner funnel. An initial temperature of 50°C. was found to be best. Doubling the amount of stabiliser did not appreciably increase the stability of the mixture.

Other variations included running the cold stabilised latex and hydrochloric acid mixture into the nitric acid at 80°C. This was fairly successful; the product looked more granular but was easily pressed to a fine powder. Inter-changing the acids and running a latex-nitric acid mixture into hot hydrochloric acid was unsuccessful, a mixture of brown and yellow granules being produced. The stabiliser sold as "Vulcastab" was found to be suitable but "Vultamol," casein and saponine were not.

The Reaction

Goldschmidt's equations for the reaction between nitric and hydrochloric acids in the presence of water are given below but these do not fully represent the more complex reactions which occur (Mellor 1922).



The reagents present provide possibilities for numerous reactions with rubber; Baker (1938) has produced products with nascent chlorine under similar conditions; nitrosyl chloride will also attack the double bonds of the rubber molecule and the acids are possible additive groups. In addition, oxides of nitrogen and products of side reactions not represented by the above general equations are likely still further to complicate the reaction.

Properties of the Product

The product is a yellowish-brown free-flowing powder having more than double the weight of the original rubber in the latex. Ultimate analyses have not been made but chlorine was estimated in the Parr Bomb and nitrogen by Kjeldahl; typical results are N=5.3 per cent, Cl=26.1 per cent. It has not been ascertained whether the stabiliser contributes to the yield but if it does not the oxygen content of the product should be of the order of 20 per cent.

The powder is insoluble in water and sodium carbonate solution but soluble in caustic soda solution, changing to a dark brown on contact with the alkali. It is insoluble in dilute sulphuric acid but dissolves in the cold concentrated acid without decomposition. In aqueous ammonia it is only partially soluble and when filtered the residue on the filter paper dissolves in acetone but gives a much darker solution than the original powder. It does not decolorise bromine in carbon tetrachloride solution.

On warming to 80°C. the product softens and can be pulled out into brittle threads, but at 130°C. thermal decomposition sets in with rapid generation of heat and carbonisation of the mass.

The following is a table of solubility in organic solvents:—

Solvent	Solubility
1. Acetone	Soluble
2. Ethyl Acetate	Soluble
3. Ethyl lactate	Soluble
4. Butyl phthalate	Soluble
5. Ethylene glycol mono- ethylether	Soluble
6. Triacetin	Soluble
7. Cyclohexanone	Soluble
8. Amyl Acetate	Small insoluble portion

Solvent	Solubility
9. Butyl Acetate (iso)	Small insoluble portion
10. Butyl Acetate (normal)	Small insoluble portion
11. Tri cresyl phosphate	Small insoluble portion
12. Ethyl alcohol	Partially or slightly soluble
13. Cyclohexanol	Partially or slightly soluble
14. Amyl acetate	Partially or slightly soluble
15. Chloroform	Partially or slightly soluble
16. Ether	Insoluble
17. Petroleum ether	Insoluble
18. Benzene	Insoluble
19. Toluene	Insoluble
20. Xylene	Insoluble
21. Cyclohexane	Insoluble
22. Dekalin	Insoluble
23. Tetralin	Insoluble
24. Carbon tetrachloride	Insoluble
25. Trichlorethylene	Insoluble
26. Tetrachlorethane	Insoluble
27. Monochlorbenzene	Insoluble
28. Carbon di-sulphide	Insoluble

After storage for two years a slight acid odour and a darkening in colour is noticeable but the general properties of the powder appear to be unchanged. Numerous possible technical applications appear to be worthy of investigation.

Literature Cited

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|---------------------|-----|-----|--|
| BAKER H. C. (1938) | ... | ... | <i>Proc. Rubber Techn. Conf.</i> 209 |
| SIBLEY R. L. (1941) | ... | ... | <i>India-Rubber J.</i> 101 13 |
| MELLOR J. W. (1922) | ... | ... | <i>A Comprehensive Treatise on Inorganic and Theoretical Chemistry</i>
2 30 |