

This work was made possible by grants from *Statens naturvetenskapliga forskningsråd* to S. Stållberg-Stenhagen. The hospitality of *AB Hässle* is gratefully acknowledged.

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Received May 11, 1959.

The Deswelling Action of Hydrazine on Nitrile Rubber

SVEN SÖNNERSKOG

A-B Svenskt Konstsilke, Borås, Sweden

In a previous paper¹ an outline was given of the primary and side reactions taking place when hydrazine or hydrazine hydrate reacts with linear homopolymers of acrylonitrile. Favourable conditions were found in homogeneous systems, as indicated by gel formation and disappearance of the strong infrared band at $2\ 260\text{ cm}^{-1}$, measuring the amount of nitrile groups in the sample. The primary polymer particle does not show this high degree of accessibility, but insolubilization occurs in both cases due to formation of interlinking units between macromolecules. The interlinking structural unit is 4-N-amino-1,2,4-triazole.

Such a reactivity is not found in copolymers of acrylonitrile and butadiene. Still more, *solubility* is limited already by the formation of microgel in the growing polymer particle at increasing degree of conversion during polymerization. Standard nitrile rubber latex with an acrylonitrile content of 37–40% dissolves in acetone, cyclohexanone or dioxane, yet with difficulty. The last mentioned solvent, however, shows a low solvent power, why phase separation instantly takes place when hydrazine is added (three phases!). Acetone and cyclohexanone are obviously unsuitable due to their reactivity.

A convenient way to study the action of an aqueous solution of hydrazine hydrate on the polymer is simply to add said reagent into a nitrile rubber latex with a low particle size. Commercial grades of butadiene-acrylonitrile latices are available for this purpose, e.g. Hycar Latex 1561, showing a medium particle size of 500 Å. The change of solubility characteristics can be observed at arbitrary intervals by casting a rubber film, preferably at reduced pressure or in a stream of dry nitrogen, followed by thorough washing in distilled water, soaking in acetone (if possible) and drying at 80°C in an inert atmosphere before use.

The weight swelling ratios of such a rubber film in a selected series of swelling agents is shown in Table 1. The degree of swelling is — rather arbitrarily — measured after an immersion time of 24 h in a large excess of liquid.

Table 1. Weight swelling ratios of nitrile rubber films, prepared at room temperature from a latex showing a solid content of 0.25 g.ml⁻¹. Conc. of hydrazine hydrate: 0.85 g.ml⁻¹. All samples preextracted in acetone at room temperature and dried at 80°C one hour before use. Time of reaction in the rubber latex: 24 h. Grade of nitrile rubber: High acrylonitrile content (37–40%), density in pure state 1.00, medium particle size 500 Å.

Swelling agent	Weight swelling ratio, g/g
Benzene	3.15
Toluene	2.82
Xylene (techn. grade)	2.25
Cyclohexane	1.10
Dipentene	1.52
Decalin	1.17
Chlorobenzene	6.77
Pyridine	8.42
Dioxane	4.92
Acetone	3.93
Cyclohexanone	8.08
2-Pyrrolidone	5.82
Dimethylformamide	7.61
Dimethylsulfoxide	4.73

A glance at the figures in Table 1 makes evident that the degree of swelling is qualitatively related to the molar volume of the solvent and its specific interaction coefficient with parent polymer. Such a

relation is strictly valid for isotropic swelling of nonionic networks, why an obvious conclusion would be to anticipate the existence of some kind of crosslinking, at least partly responsible for swelling behaviour. As a pure thermal curing reaction at the carbon-carbon double bonds must be excluded at the low temperature in question, only two cases can be considered, *viz.*

- a. Reaction between hydrazine hydrate and nitrile groups at the polymer-water interface.
- b. Formation of a highly active redox system between hydrazine hydrate and activator residues, capable of initiating a continued polymerization (crosslinking) to a low extent.

Said types of reaction are mutually independent but cooperate in reducing the degree of swelling of the copolymer. As the parent polymer itself shows only a moderate affinity to solvents cited above, a very slight degree of crosslinking or reduction of the number of solvogenic groups would be sufficient to produce a gel fraction. In fact the infrared spectrum of cured rubber films gives no definite information of chemical changes but a new band at $3\ 250\ \text{cm}^{-2}$, possibly due to formation of amide groupings.

An increase of reaction temperature to 80°C , as well as a prolonged time of curing, does not principally change the swelling behaviour. This remarkable insensitivity would be unintelligible if the curing effect were solely caused by a propagating chain reaction within the polymer particles, initiated by free radicals at the polymer-water interface. It is easily demonstrated that addition of a reactivating system, such as potassium persulphate-sodium pyrosulphite to a rubber latex, buffered with sodium carbonate-sodium bicarbonate, causes a gradual deswelling of the polymer due to crosslinking at the carbon-carbon double bonds. The rate is dependent of temperature and concentration of initiator. Analogous experiments on emulsions of butadiene-styrene copolymer have been reported ².

Scope of reaction in anhydrous systems. A carefully purified and dried rubber film reacts with anhydrous hydrazine at elevated temperature. A gradual deswelling takes place at 80°C , as seen from Table 2. The rate of deswelling rapidly decreases after 24 h. The reaction is too slow at room temperature to be practically applicable.

Table 2. Weight swelling ratios of nitrile rubber films, prepared at room temperature, purified in water, dried in a current of carbon dioxide, cured in a large excess of anhydrous hydrazine at 80°C . Swelling agent: dioxane. Temperature of swelling: 20.0°C .

Time of curing, h	Weight swelling ratio, g/g
12	4.32
24	3.74
48	3.45
72	3.24
120	3.18
144	3.00
168	2.94

The cured films were not preextracted in acetone before use, because a preliminary test revealed no significant amount of soluble polymer. Remaining hydrazine in the samples was removed by soaking in methanol, followed by drying *in vacuo* for 48 h. During this drying operation a distinct pink color is gradually developed in the specimens. The intensity is related to the time of curing. This color formation is wellknown from the reaction between hydrazine and homopolymers of acrylonitrile ¹.

Deswelling of a rubber film merely by heating in air at the actual temperature gives a limiting swelling ratio of 10.27 after 168 h (preextracted sample). A blank, heated in dry carbon dioxide gas in the same way, is too readily redispersed in the swelling agent to be used for quantitative measurements. Even an immersion of a film in 0.1 M potassium persulphate solution for an identical period gives a moderate decrease of swelling (weight swelling ratio = 7.92, preextracted sample). It is apparent that contributions from chemical reactions between polymer and hydrazine are of primary importance in reducing swellability. Work is continued to find more favourable working conditions, as infrared spectra also in this case give but scanty information on the extent of conceivable reactions.

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Received May 12, 1959.