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Ultrastructure of Rubber Particles in PA 80 Latex. II. Effects of Storage

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As a result of the sensitivity of PA 80 latex to 5% $KMnO_4$ fixation in differentiating vulcanised and unvulcanised particles or zones of these particles, this method was again used to find the effects of storage. Latices examined were from various stages of vulcanisation which have been stored for one and six months.

Vulcanisation as judged from the increase in intensity of staining of the particle interior was found to be progressive during storage even when the stage of vulcanisation was preliminary i.e. *when the dispersion mixture was just added. The shell thickness of the rubber particles too is increased. Evidence from elsewhere has shown that there is an increase in free and total sulphur and gel content on storage. The electron microscopic results are consistent with these findings.*

Even though all the specification limits have been met at the producers' level, there are still some complaints from local as well as overseas users of PA 80. Most of the complaints relate to the calendered product of PA 80 having poor surface finish and often displaying discrete lumps of uneven dispersion[1].

Storage may have contributed to the problems encountered especially during the long course of transportation or shipment. It is with this problem in mind that this study was undertaken. The effect of storage of PA 80 latex is also studied for fundamental reasons, despite the fact that PA 80 may not be exported in that form any more. The changes detected, as in an earlier study[2] have managed to differentiate and in some ways, explain what happens during storage. Observations are made on one and six months' storage under controlled conditions.

MATERIALS AND METHODS

The same latex samples that were used in the last study[2], collected at the various stages of vulcanisation, were kept at room temperature. These were sampled one and six months later for electron microscopy. Samples were subjected to similar procedures for electron microscopic examination as described earlier[2].

OBSERVATIONS AND DISCUSSION

Osmium Fixation

In general, osmium fixation did not seem to show distinctive differences in the microstructure of the rubber particles when these different samples were stored. It is however worthy to note that there are changes in the ammoniated sample especially that which has been stored for six months. As has been shown previously[2], the addition of 0.7% NH_3 to latex affected the elasticity of the membrane of the rubber particles *i.e.* there was a change from a rigid boundary to a crenulated one.

On storage, the boundaries of the rubber particles still remained crenulated perhaps less; but not all the particles were showing uniform electron density *(Figure 1B)*. These odd particles have electron density grading from darker in the periphery to lighter in the interior. There are even some particles which contain fibrillar material within the empty-looking interior. These are reminiscent of the lipid particles in their different stages of formation in the Frey-Wyssling (F.W.) complexes[3]. The crescent-like particle in *Figure 1B* is most probably a component from a broken F.W. complex.

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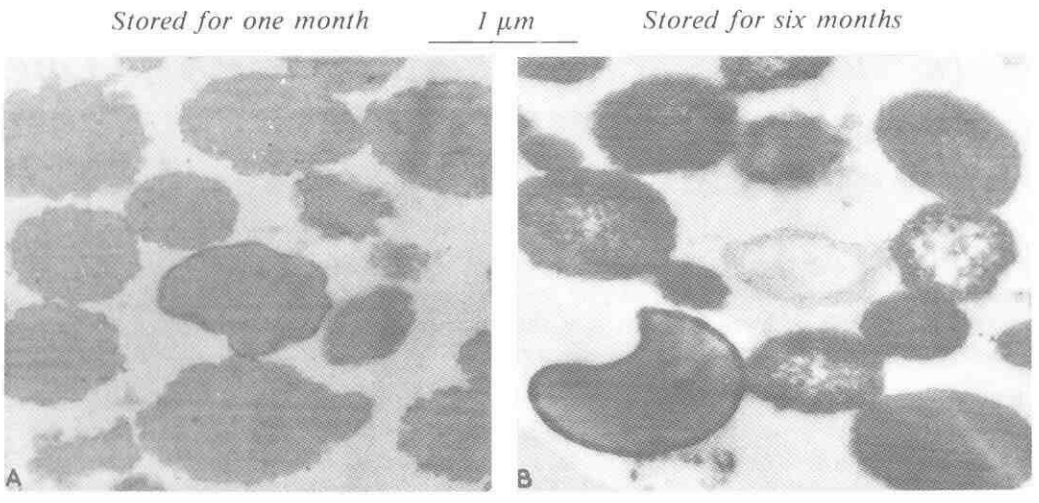

Figure 1. Sections of 0.7% ammoniated rubber particles stored for one month and six months; fixed in OsO_4 and stained in lead citrate.

Permanganate Fixation

$KMnO_4$ fixation was found to be the more sensitive fixative in detecting micro-structural changes in rubber particles during sulphur vulcanisation[2]. Only the stained sections are discussed here as they are enhanced further by the addition reaction of osmium tetroxide.

The stored ammoniated rubber particles are shown in *Figures 2A* and *2B*. Gross changes were not apparent in these rubber particles but there is an indication of a slight increase in the shell thickness at six months' storage (an increase of approximately 1000 Å from the one-month storage in the limited number of particles measured). It is possible that this increase in shell thickness is somewhat related to the change in composition of membrane or related structures of stored ammoniated latex as some studies have indicated[4]. Stored ammoniated latex has also been shown to have an increase in the MST[5].

What is interesting at the 0-h stage (*i.e.* immediately after adding the vulcanising dispersion) is the speckled interior of these particles ranging from a few dots in the one-month stored sample *(Figure 2C)* to a visible speckled-ball in the six-month stored sample *(Figure 2D)*. This speckled interior in the unstored sample was only seen 2 h after putting the steam on *i.e.* at 77°C. With this observation, it can be inferred that vulcanisation is still taking place during storage, based on the resistance of the particles to oxidation by permanganate during the fixation procedure.

Another feature at the 0-h stage, not generally observed in the unstored sample, is the rupturing of the particle shells (representing the gel layer), especially in the bigger particles and in the six-month stored sample (*Figures 2C* and *2D*). This may have been attributed partly to the brittleness of the shell and also to the swelling of the sol in the embedding medium as a result of being only partially vulcanised. Fresh, unvulcanised rubber particles fixed in $KMnO_4$ also sometimes experience shell rupture, but this is not excessive and is mainly considered to be due to the fixation releasing some gaseous by-products of the oxidation reaction.

As the process of vulcanisation progresses, the intensity of the interior of the shell increases proportionately; but more intensely in the six-month stored 80:20 mixture *(Figure 2P)*. This means that these latter particles are more vulcanised than the one-month sample. Other features which are also indicative of being more vulcanised are the almost intact shell, perhaps

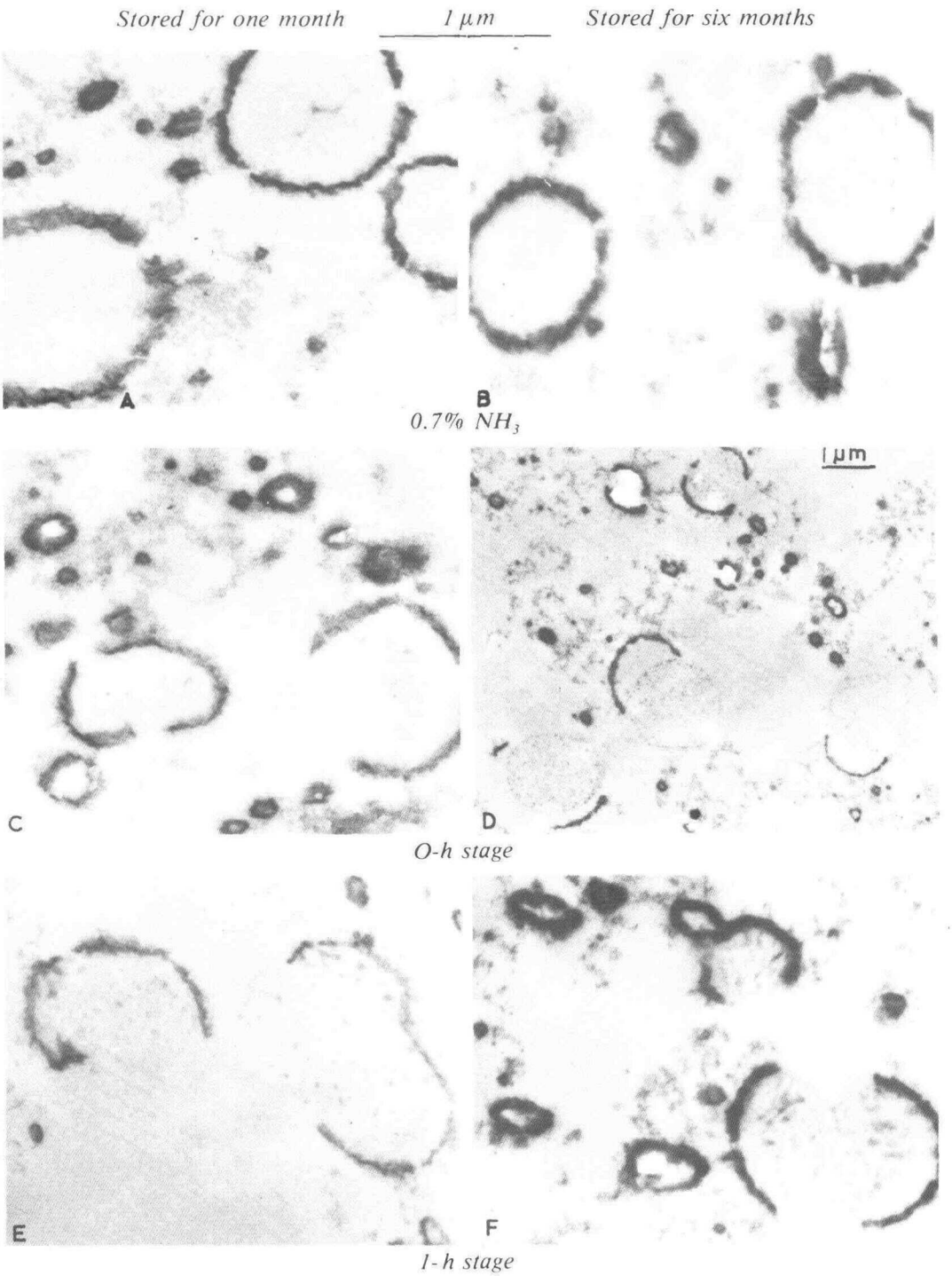

Figure 2. Sections of stored (one and six months) rubber particles from various stages of vulcanisation; fixed in $KMnO_4$ and post-stained with osmium vapour.

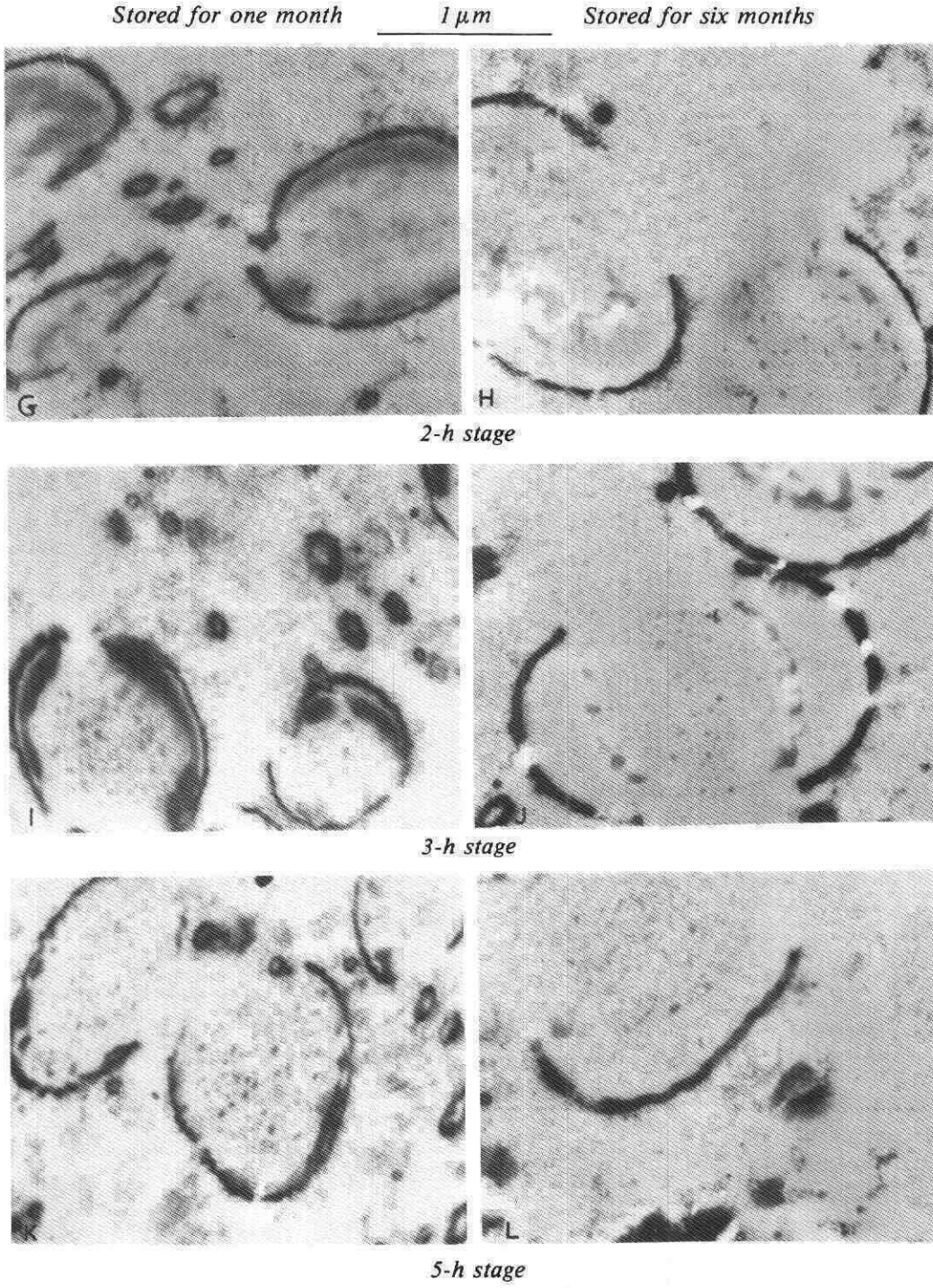

Figure 2. Sections of stored (one and six months) rubber particles from various stages of vulcanisation; fixed in $KMnO_4$ and post-stained with osmium vapour (contd).

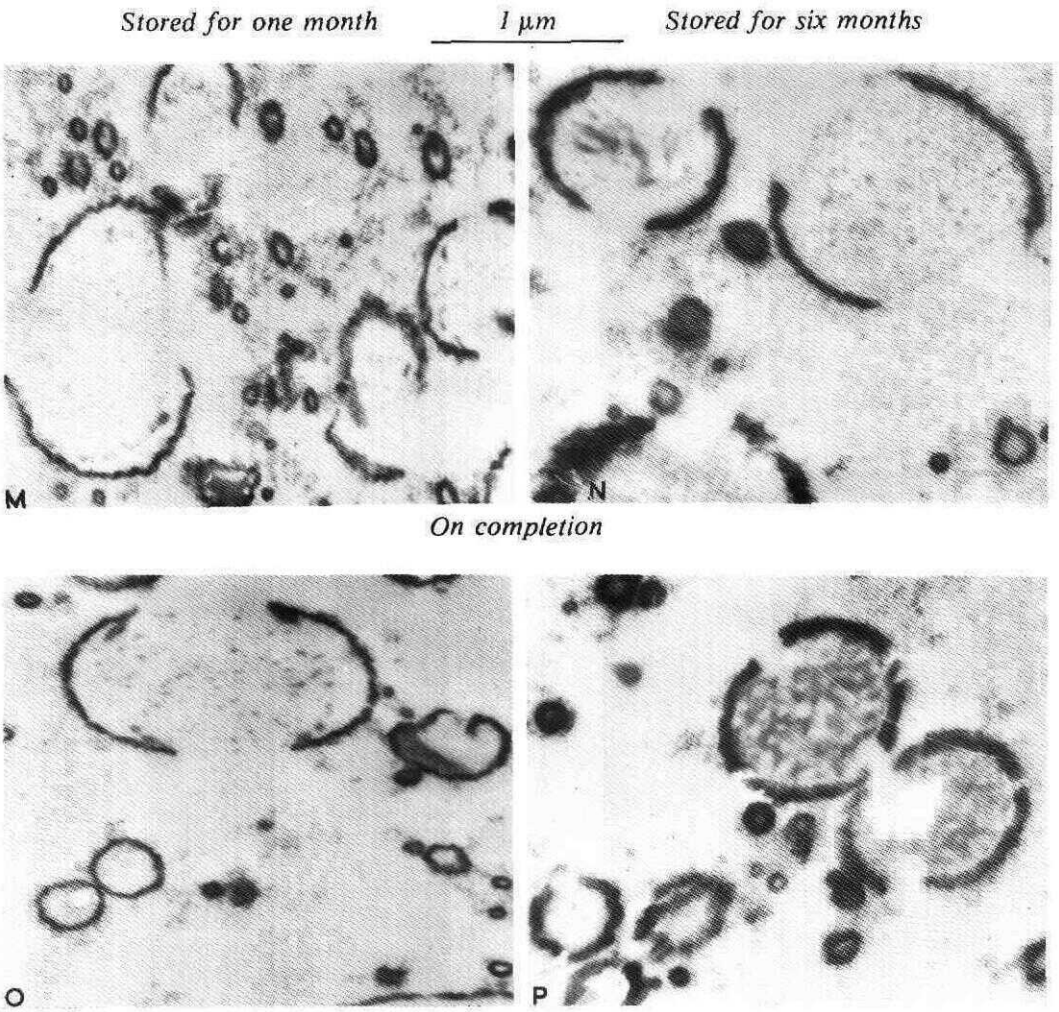

Figure 2. Sections of stored (one and six months) rubber particles from various stages of vulcanisation; fixed in $KMnO_4$ and post-stained with osmium vapour (contd).

with a small rupture, and close adherence of sol to gel (shell) indicating no swelling or limited swelling.

In the other stages of vulcanisation, rupturing of the shell is also extensive especially in the six-month stored samples. The limited shell rupture in the one-month stored sample (from the 2-h stage to the 5-h stage) is probably due to the presence of an electron-dense band very close to the shell (*Figures 2G, 2I* and *2K*). This may represent the external part of the sol which is highly vulcanised, compared to the interior, which did not succumb to swelling. Such bands are, however, not clearly seen in the six-month stored samples.

Storage has also an effect on the shell thickness of the rubber particles sampled during the various stages of vulcanisation. The thick-

ness of the shell after six months' storage (average of 650 Å) shows an increase over the unstored samples (average of 400 Å) and one-month stored samples (average of 200 Å). What is implied by the increase in thickness of the shell may well have been related to the increase in gel content as shown by *Table 1*. Even though these values were not obtained from the experimental samples (from a commercial factory) yet the values do show an increase on storage. The increase in free sulphur and total sulphur on storage as shown in this table could also be related to the increase in intensity of the internal sol observed as the samples were stored.

TABLE 1. EFFECTS OF STORAGE ON THE PHYSICAL PROPERTIES OF PA 80 LATEX[a]

Property	Storage		
	0 month	3 months	6 months
Mooney viscosity, V_R	71.7	71.7	78.7
Swell (%)	8.8	9.7	9.1
Gel content	82.7	84.9	85.5
Free sulphur (%)	0.3	0.4	NA
Total sulphur	1.6	1.7	NA

NA = Not available

[a]Values derived from means of three samples made from one lot (batch).

CONCLUSION

The increase in the intensity of staining of the electron-dense specks within the shells of the $KMnO_4$ fixed stored samples could be envisaged as an increase in the degree of vulcanisation and consequent increase of crosslink density. It is interesting to note that with greater duration of storage, the inner part of the rubber particle not only has a higher electron density but is more resistant to permanganate oxidation under the conditions it is exposed to. This is consistent with the hypothesis that storage increases the degree of vulcanisation of each particle presumably due to the residual effects of the vulcanising dispersion present in the mixture. Probably, savings on chemicals could be effected by a finer degree of control on the dispersion mixture.

The study also demonstrates that the permanganate fixation technique is a sensitive technique for electron microscopic examination of rubber particles subjected to modification by vulcanisation and similar phenomena.

This study is limited to stored latex in the vulcanised form and does not throw light on the effects of vulcanisation and subsequent processing of rubber on the conditions of storage. For example, it does not throw light on the crepe or block rubbers made from PA 80. It is suggested that such a study may have inherent values associated with it.

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