LETTERS TO THE EDITORS

The Protection of Transparent Vulcanizates Against Ageing in Sunlight

Care has to be taken in choosing antioxidants for use in transparent natural rubber vulcanizates since some amines commonly employed as protective agents against thermal degradation photosensitize ageing in ultraviolet (uv) light.[1] Further studies[2] using the technique of stress relaxation, undertaken in order to find the most satisfactory type of antioxidant for protection against sunlight ageing, have shown that, with additives introduced into extracted samples of peroxide vulcanizate by swelling from ethyl acetate solution, the best results were obtained using a mixture of a substituted bis-phenol and an absorber of uv light. Hitherto, nickel isopropylxanthate (NPX) has been regarded as the most potent protective agent against light;[3] however, the rate of degradation in the presence of NPX was unchanged by the addition of uv absorber and the mixture of bis-phenol and absorber was markedly more effective. Furthermore, the nickel salt is green, whereas the bis-phenols are relatively nonstaining.

The work described here is an evaluation of vulcanizates in which the phenol and absorber have been incorporated before cure. The phenol employed was 2,2'-methylene-bis(4-methyl-6-tert-butyl phenol) (Antioxidant 2246 of the American Cyanamid Co.) and the absorber was Tinuvin P (a product of undisclosed formula marketed by Geigy Ltd.), chosen since it protected better in the absence of antioxidant than two other commercial absorbers. Two types of transparent vulcanizate were examined, one being an accelerated sulfur cure and the other a dicumyl peroxide cure. The recipes were as follows:

Sulfur Vulcanizate. Pale crepe 100, sulfur 2, "transparent" zinc oxide 1, TMT 0.2, TET 0.3, Antioxidant 2246 1, cured 20 minutes at 140°C.

Peroxide Vulcanizate. Pale crepe 100, Dicup 3, Antioxidant 2246 1, cured 60 minutes at 140°C.

Vulcanizates were prepared according to these recipes both with and without 2 parts of Tinuvin P added before vulcanization; the addition of Tinuvin P had no effect on tensile properties. The samples for examination by measurement of stress relaxation were vulcanized in a mold designed to give sheets 0.2 mm. thick while the samples for exposure to sunlight were 2.5 mm. thick.

Stress relaxation, which measures directly the relative amount of breakdown of the rubber network, was carried out in air at 25°C. under irradiation with the light of wavelength 313 mμ and greater emitted by a high pressure mercury lamp. Tinuvin P brought about a marked decrease in the rate of degradation both in the peroxide and the sulfur vulcanizate, particularly in the latter case (Fig. 1). When the protective agents were the same, the sulfur vulcanizate was found to be photochemically degraded far more rapidly than the peroxide vulcanizate. An auxiliary experiment, in which an antioxidant less stable in light, 2,5-di-tert-amylhydroquinone (Santovar A of Monsanto Ltd.), was introduced with and without Tinuvin P into a
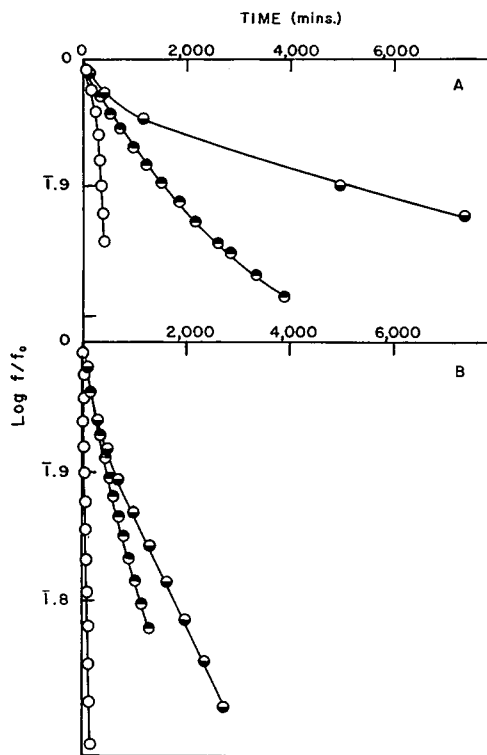

Fig. 1. Stress relaxation at 25°C. in uv light of (A) dicumyl peroxide and (B) sulfur-accelerator vulcanizates. (O) Extracted control. (◑) With 2246 only. (◓) With 2246 and Tinuvin P.

peroxide vulcanizate by swelling from ethyl acetate solution, showed that the uv absorber prolonged the life of the antioxidant as well as lowering the rate of degradation of the vulcanizate. In absence of both 2246 and Tinuvin P (removed by extraction) degradation was extremely rapid.

Similar samples both of the peroxide and the sulfur vulcanizate to those subjected to photochemical degradation were examined by stress relaxation in air at 100°C., and Tinuvin P was found to have no effect on thermal ageing. The thermal ageing of the peroxide vulcanizate was much better than that of the sulfur vulcanizate.

Sunlight ageing of these materials was carried out in racks on the laboratory roof, with the samples facing south and at an angle of 45° to the vertical. They were exposed, unstrained, for 8 weeks in summer (approximately 400 hours sunshine). The results obtained are in accord with those obtained by stress relaxation and are illustrated by photographs (Fig. 2) in which the samples have been slightly bent so as to enable the cracking pattern to be more clearly seen. After exposure the Dicup stock containing Antioxidant 2246 and Tinuvin P was in excellent condition, showing only slight crazing, while in absence of Tinuvin P the degree of crazing was more serious. Fine crazing of the
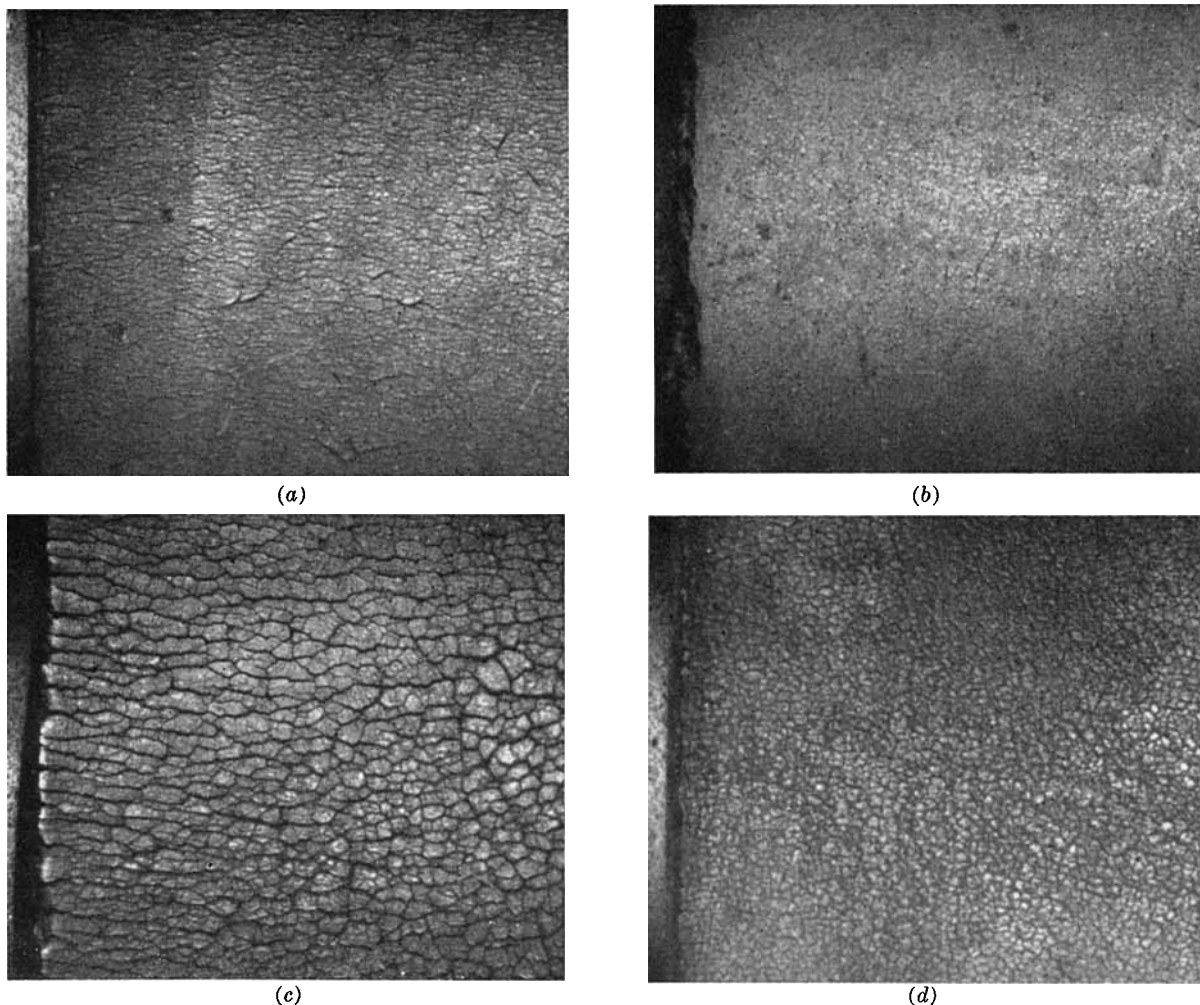
Fig. 2. Appearance of vulcanizates after 8 weeks in sunlight. (*a*) Dicumyl peroxide vulcanizate with 2246 only. (*b*) Dicumyl peroxide vulcanizate with 2246 and Tinuvin P. (*c*) Sulfur accelerator vulcanizate with 2246 only. (*d*) Sulfur accelerator vulcanizate with 2246 and Tinuvin P.

sulfur stock occurred in presence of Antioxidant 2246 and Tinuvin P, while in absence of the absorber very pronounced crazing had occurred.

It is suggested that a combination of uv absorber and non-staining antioxidant effectively protects transparent vulcanizates against sunlight ageing. In filled stocks the absorber is not so useful since the filler itself acts as a light screen.

References

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Control of Temperature Rise in Crosslinking of Unsaturated Polyesters by the Use of Gamma Radiation Initiation

Introduction

Schulz[1] and others have shown that the kinetics of free-radical initiated vinyl polymerization follow the kinetic equation

$$dM/dt = K_1[C]^{1/2} [M] [K_2M/(1 + K_2M)]^{1/2}$$

Matheson[2] in a subsequent paper gave theoretical justification for this behavior on the basis of a "cage effect." The following reactions were assumed to take place

(1) $(RCOO)_2 \xrightarrow{k_2} 2RCOO\cdot$ $r = k_1 ([RCOO])_2$

(2) $RCOO\cdot + RCOO\cdot \xrightarrow{k_2} (RCOO)_2$ (cage effect)
$$r = k_2 [RCOO\cdot]$$