

Identification of bloom on vulcanisates by thin-layer chromatography

During vulcanisation studies of ethylene-propylene terpolymers, the formation of a bloom was noted when certain cure systems were used. It was suspected that the cause of this bloom was due to the insolubility of some accelerators or their derivatives formed during the vulcanisation process. A simple and rapid procedure was therefore required, to examine the bloom of which only microgram quantities of material were usually available. Thin-layer chromatography was therefore chosen as being a suitable technique. Identification by R_F values and characteristic colour reactions were made easier by the fact that the nature of the starting materials was known and the resulting chromatograms could be interpreted by comparison with a limited number of known reference substances.

Chromatographic systems for the identification of certain rubber compounding ingredients, including accelerators, have been evaluated by KREINER AND WARNER¹ and use of these systems was made during the present work.

Experimental

Removal of bloom. Two methods of removing the bloom from the surface of the vulcanisate were tried:

(a) A portion of the bloom was scraped off with a razor blade and the scrapings were dissolved in chloroform.

(b) A portion of the bloom was removed by swabbing the surface of the vulcanisate with cotton-wool soaked in chloroform. The cotton-wool was then extracted with chloroform in a Soxhlet extraction thimble and the extract was concentrated by evaporation.

The latter method was found to be the most convenient for this work.

Preparation of plates. The plates used were 20 × 20 cm plates coated to a thickness of 250 μ with Merck Silica Gel G using the standard Desaga equipment. The plates were allowed to dry by standing in the open laboratory overnight, and were then used without any further activation.

Solvent system. Benzene-ethyl acetate-*n*-butanol (50:1:1, v/v) was used as the solvent system, as suggested by KREINER AND WARNER¹.

Revealing reagents. The following revealing reagents were used:

(a) *Dithizone.* 0.05 g dithizone were dissolved in 100 ml carbon tetrachloride. Zinc-containing compounds show up as pink spots on a green background.

(b) *Palladium chloride.* 0.5 g palladium chloride was dissolved in 50 % aqueous acetone and acidified by the addition of a few drops of hydrochloric acid. Sulphur-containing compounds show up as brown spots on a yellow background.

(c) *Phosphomolybdic acid.* 5 g phosphomolybdic acid were dissolved in 100 ml isopropanol. Spraying with this reagent is followed by short heating of the plate at 110° when reducing compounds show up as blue spots on a yellow background.

Reference solutions. 1 % solutions in chloroform of each of the following accelerators were prepared: Mercaptobenzthiazole (MBT), tetramethylthiuram disulphide (TMTDS), tetraethylthiuram disulphide (TETDS), zinc dimethyldithiocarbamate (ZDMDC), zinc diethyldithiocarbamate (ZDEDC), zinc benzothiazyl sulphide (ZMBTS), tetramethylthiuram monosulphide (TMTMS) and benzothiazyl disulphide (MBTS).

Procedure. 5 μ l portions of each of the bloom extracts, together with 5 μ l portions of each of the reference solutions were applied, using a 10 μ l Hamilton microsyringe, as a series of spots along one edge of the plate. The chromatogram was developed until the solvent had advanced 10 cm up the plate. Unlined tanks were used to obtain maximum resolution.

Results and discussion

The accelerators used in the first sample (sample A) to be studied were MBT, TMTDS and TETDS. It was considered that the bloom might contain any of these or their zinc salts that might have been formed during the vulcanisation process, *i.e.* ZDMDC, ZDEDC and ZMBTS—the zinc having originated from zinc oxide present in the original cure system. Sample B originally contained TMTMS and MBTS and possibly ZDMDC formed during vulcanisation.

Fig. 1 shows a TLC chromatogram of the eight reference materials (spots 1–8), sample A obtained by scraping (spot 9), sample A obtained by swabbing (spot 10) and sample B obtained by swabbing (spot 11). This chromatogram was obtained by spraying with the palladium chloride reagent. An identical chromatogram was obtained by spraying with the phosphomolybdic acid reagent which is a general revealing agent. The fact that the two chromatograms were identical suggested that all the spots were sulphur compounds. Fig. 2 is a similar chromatogram sprayed with dithizone. This showed up the zinc-containing materials as pink spots on a green background. Most of the other materials showed up as yellow spots.

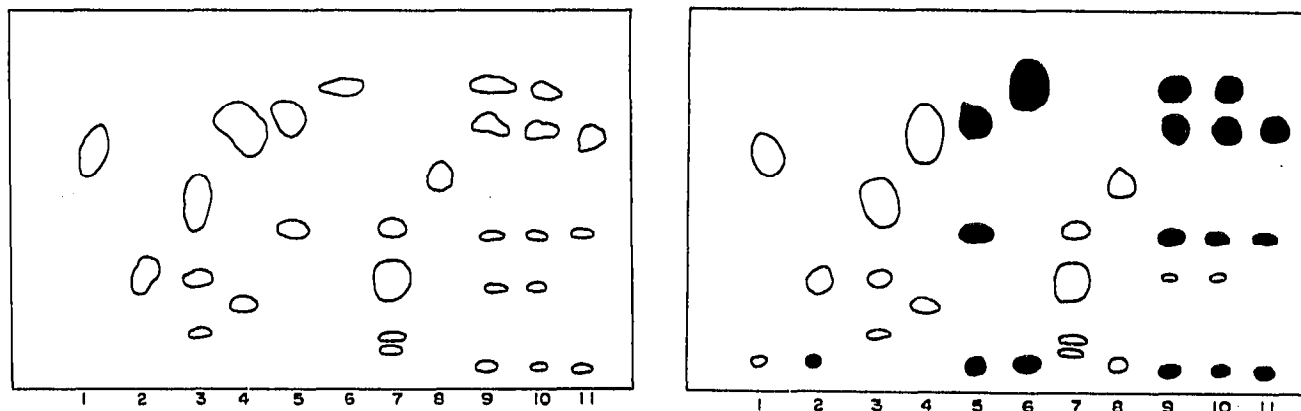


Fig. 1. TLC chromatogram on Silica Gel G. Solvent system benzene-ethyl acetate-*n*-butanol (50:1:1, v/v). 1 = MBT; 2 = ZMBTS; 3 = TMTDS; 4 = TETDS; 5 = ZDMDC; 6 = ZDEDC; 7 = TMTMS; 8 = MBTS; 9 = sample A removed by scraping; 10 = sample A removed by swabbing; 11 = sample B removed by swabbing. Revealing reagent: palladium chloride.

Fig. 2. Similar chromatogram to Fig. 1 but revealed by spraying with dithizone reagent. Shaded spots: pink; clear spots: yellow.

By examining these chromatograms it can be seen that: (a) None of the reference standards were pure materials. (b) Spots 9 and 10 show the two methods of extracting the bloom were equally suitable for TLC purposes, since they gave rise to identical chromatograms. Swabbing with cotton-wool soaked in chloroform was used in all subsequent work since this was found to be the more convenient method. (c) The bloom from sample A (9, 10) consisted of ZDMDC (5) and ZDEDC (6) in roughly

equal proportions together with a small amount of ZMBTS (2). TMTDS (3), TETDS (4) and MBT (1) were not present. (d) The bloom from sample B (11) consisted entirely of ZDMDC (5). No TMTMS (7) or MBTS (8) was found.

Conclusions

Thin-layer chromatography is a rapid and simple technique for identifying accelerators and some of their reaction products in samples of bloom removed from ethylene-propylene terpolymer vulcanisates by extraction with cotton-wool soaked in chloroform.

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1 J. G. KREINER AND W. C. WARNER, *Am. Chem. Soc. Div. Rubber Chem., Spring Meeting, Miami Beach, May 4-7, 1965*, Paper 4.

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