

CHROM. 7065

Note

Detection of hexamethylenetetramine in vulcanizates

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Hexamethylenetetramine (hexa) is commonly used as a methylene donor in the resorcinol-formaldehyde bonding systems which are often employed in tire vulcanizates. These bonding systems enhance the adhesion obtained between the rubber and cord elements of a tire. A small amount of undecomposed hexa remains in the rubber after vulcanization¹. This residual hexa can be efficiently removed from the cured rubber by extraction with chloroform. A large number of other rubber additives are also extracted by chloroform; however, the solubility of hexa in water (46% by wt.) makes it possible to selectively extract ample hexa from the chloroform for thin-layer chromatographic (TLC) identification.

Resotropin, a reaction product of hexa and resorcinol, is also used as a bonding agent in vulcanizates². A cured rubber containing resotropin yields free hexa upon extraction and cannot be differentiated from those originally compounded with hexa.

EXPERIMENTAL

Five grams of finely cut vulcanizate were extracted 2 h in a soxhlet apparatus with chloroform. The extract was concentrated to less than 25 ml, transferred to a 25-ml volumetric flask and diluted to volume with chloroform. One-half ml of water was added, the flask stoppered, vigorously shaken several times during a 15- to 20-min period and then allowed to stand until the water layer reformed. A capillary-tipped medicine dropper was used to remove the clear portion of the water layer for TLC analysis.

Activated silica gel G layers (standard thickness 250 μm) were used for TLC analysis. Five μl of the clear water solution was applied to the layer and eluted 15 cm in a filter-paper lined tank containing methanol-conc. ammonium hydroxide (9:1). After development the air-dried layer was sprayed with chromotropic acid solution and placed in an oven at 110° for 15 min. The hexa was observed as a blue-violet spot on a light blue background at an R_f of 0.45. The chromotropic acid solution was prepared by mixing 5 parts of 60% sulfuric acid with one part of aqueous 10% 4,5-dihydroxy-2,7-naphthalenedisulfonic acid³. Five μl of a 0.25% solution of hexa in water was used as a standard.

RESULTS AND DISCUSSION

This method has been successfully tested on several known control vulcanizates without complication. The control compounds contained either hexa, resotropin or one of three other commercially available methylene donors. The water extraction selectively removed the hexa from the chloroform extract and left behind other ingredients that might have interfered with TLC detection. Since hexa releases formaldehyde in acid media, chromotropic acid, a specific and sensitive indicating reagent for formaldehyde, was employed. The resotropin-containing vulcanizates yielded large quantities of hexa and could not be differentiated from vulcanizates compounded with straight hexa. No meaningful responses were observed for the other methylene donors.

REFERENCES

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