

LETTERS TO THE EDITORS

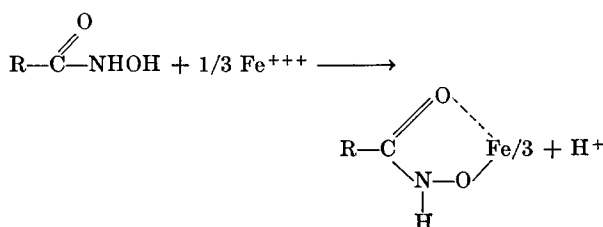
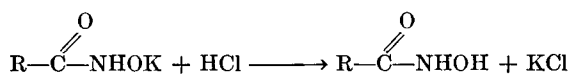
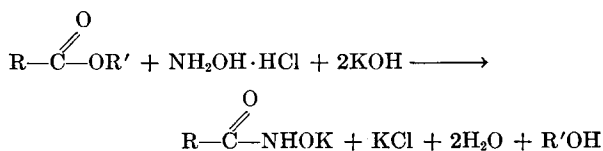
Colorimetric Differentiation of Polyester- and Polyether-Based Urethane Polymers

Urethane polymers, such as flexible and rigid foams, elastomers, various coatings, and adhesives, are formed by polyaddition polymerization of diisocyanates and polyhydroxyl compounds. In practically all commercial applications either polyesters or polyethers are used as hydroxyl terminated compounds. A quick, qualitative differentiation between urethane polymers based on polyesters and those based on polyethers is highly desirable because the successful application in special cases may depend on this knowledge and may save a large number of mechanical tests or a fairly complicated saponification followed by a more difficult determination of the hydrolysis products.

A general analytical method for the detection of polymers containing urethane groups was recently published.¹

Qualitative Color Test for Polyesters^{2,3}

The colorimetric test is based on the following reactions, where R and R' are di- or poly functional:



The hydroxamic acid from the polyester reacts with the ferric ion to form an inner complex salt which is water-soluble and of an intensive violet or purple color for most hydroxamic acids.

Reagents

- 2 N solution of KOH in methanol plus phenolphthalein to a dark pink color.
- Saturated solution of $\text{NH}_2\text{OH}\cdot\text{HCl}$ in methanol.
- 1 N hydrochloric acid.
- 1-3% solution of FeCl_3 in water.

Procedure

Approximately 50 mg. of the polymer are cut into small pieces and reacted with a few drops of Reagent (a) and then a few drops of Reagent (b) are added. The resulting mixture must be alkaline as indicated by the phenolphthalein. Heat-

ing for 20-40 seconds to not more than 50°C. will increase the reactivity considerably but is only necessary for higher crosslinked polymers. After 30-60 seconds reaction time, the mixture is acidified with Reagent (c) and reacted with one drop of Reagent (d). In the presence of esters the characteristic violet color will appear immediately.

Discussion

This color test is only specific for polyesters if no other esters are present, as from solvent, plasticizers, or flow agents. Normally occurring functional groups in urethane polymers, such as urethane, urea, allophanate, biuret, amine, or isocyanate groups, do not interfere with the color test under the test conditions. Since ethers also will not react with hydroxylamine in this test, the polyester-based polymers can easily be differentiated from the polyether-based polymers.

Polyesters made from castor oil or dimerized fatty acids, sometimes used in urethane polymers, will give a brownish or brownish-violet color rather than the violet color. This brownish color, however, should not be confused with the yellow-brownish color resulting from the ferric chloride alone.

On some materials, such as flexible foam, the test may be carried out as a spot test directly on the foam by dropping a few drops of each of the four reagents in order. In this case the test may be made at room temperature and the color will develop immediately. The entire test requires about one minute to complete.

References

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- F. Feigl, *Spot Tests in Organic Analysis*, 5th edition, Elsevier-Van Nostrand, New York, 1956, p. 237.

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Dynamic Mechanical Properties of Graft Copolymers of Nylon

Many works^{1,2} have been devoted to the measurement of the dynamic mechanical properties of polymers in the solid state as a function of temperature for the elucidation of internal structure and atomic movement. However, studies for graft copolymers have not as yet been published. Recently a method for the preparation of graft copolymers by irradiation of ionizing radiations has been presented.^{3,4}