

phenylhydrazone radical (III) are formed by these reactions.

On dissolving in benzene, electron spin resonance singlets displayed by solid radicals become triplets similar to that of the initial ketone radical.

M. B. NEIMAN
E. G. ROZANTZEV
YU. G. MAMEDOVA

Institute of Chemical Physics,
Academy of Sciences,
Moscow.

¹ Steacie, E. W. R., *Atomic and Free Radical Reactions*, second ed. (Reinhold Pub. Corp., New York, 1954).

² Waters, W. A., *The Chemistry of Free Radicals*, second ed. (Oxford Univ. Press, London, 1948).

³ Walling, C., *Free Radicals in Solution* (John Wiley and Sons, Inc., New York, 1957).

⁴ Harries, C., and Lehmann, F., *Ber.*, **30**, 232, 2736 (1897).

Triboelectricity in Polymers

It must be emphasized that the reality of a triboelectric series implies a single determinant property acting at both donor and acceptor surfaces. An 'abundance effect'¹, if real, may be a cause of minor anomalies, but it cannot be dominant since metals, which may be inserted in the series, contain incomparably more conduction electrons than do insulators. The Frenkel mechanism² of thermal excitation alone is inadequate, since pyrolysis would occur, in the 100 μ sec suggested by Frenkel, below 500° C, at which the population of conduction electrons might well be only 100 per c.c. Since it is known that calendaring may reduce the molecular weight of polymers, I suggest that free radicals, produced by mechanical

TRIBOELECTRIC SERIES

(positive end)
Silicone elastomer with silica filler
Borosilicate glass, fire-polished
Window glass
Aniline-formol resin (acid catalysed) —CH₂—Ph—NH—
Polyformaldehyde —CH₂—O—
Polymethylmethacrylate —CH₂—CMe(COOCH₃)—
Ethylcellulose
Polyamide 11 —(CH₂)₁₀CO—NH—
Polyamide 6-6 —(CH₂)₄CO—NH(CH₂)₆NH—CO—
Rock salt Na Cl
Melamine formol
Wool, knitted
Silica, fire-polished
Silk, woven
Poly-ethylene glycol succinate —(CH₂)₂COO(CH₂)₂OCO—
Cellulose acetate
Poly-ethylene glycol adipate —(CH₂)₂COO(CH₂)₂OCO—
Poly-diallyl phthalate —CH₂CH=OCOPhCOOCH=CH₂
Cellulose (regenerated) sponge
Cotton, woven
Polyurethane elastomer —NHPhNHCOOROCO—
Styrene acrylonitrile copolymer
Styrene butadiene copolymer
Polystyrene —CH₂—CHPh—
Polyisobutylene —CH₂—CMe₂—
Polyurethane flexible sponge
Borosilicate glass, ground surface
Polyethylene glycol terephthalate —COPhCOO(CH₂)₂O—
Polyvinyl butyral
Formo-phenolic, hardened —CH₂—PhOH—CH₂—
Epoxide resin —OPhCMe₂PhOCH₂CHOHCH₂—
Polychlorobutadiene —CH₂CCl—CHCH₂—
Butadiene acrylonitrile copolymer
Natural rubber —CH₂CMe=CHCH₂—
Polyacrylonitrile —CH₂—CH(CN)—
Sulphur
Polyethylene —CH₂—
Polydiphenyl propane carbonate —OPhCMe₂PhOCO—
Chlorinated polyether —CH₂—C(CH₂Cl)₂CH₂O—
Polyvinylchloride with 25 per cent D.O.P.
Polyvinylchloride without plasticizer —CH₂—CHCl—
Polytrifluoroethylene —CF₂CFCl—
Polytetrafluoroethylene —CF₂—

stress, form a source of relatively high-energy electrons, easily excited to the conduction-level. The much-discussed charge transfer by non-rubbing contact remains improbable except between distant members of the series.

My triboelectric series of well-defined polymers shows no correlation with dielectric constant, with dipole moment, nor indeed with the colour or intensity of ultra-violet-excited luminescence, which renders unlikely the proposed role of electron traps³. Members tend to be grouped by chemical nature, pointing to a determinant property linked to molecular constitution, perhaps more particularly to that of the surface⁴. The Fermi-level remains the most reasonable series-determining property⁵.

J. HENNIKER

Centre d'Etude des Matières Plastiques,
13 rue Pierre Curie,
Montrouge,
Seine, France.

¹ Henry, P. S. H., *Brit. J. App. Phys.*, Suppl. No. 2, S 6 (1953).

² Frenkel, J., *J. Phys.* (U.S.S.R.), **5**, No. 1, 25 (1941).

³ Fukada, E., and Fowler, J. F., *Nature*, **181**, 698 (1958).

⁴ Ellison, A. H., and Zisman, W. A., *J. Phys. Chem.*, **58**, 503 (1954).

⁵ van Oostenburg, D. O., and Montgomery, D. J., *Textile Res. J.*, **28**, 22 (1958).

Complexity of Hop Oil

PROGRESS in instrumental methods of analysis during the past 10 years, particularly in the new field of gas chromatography, has provided the chemist with powerful tools for the separation and identification of complex mixtures. Nevertheless, it is often advantageous to fractionate the mixture prior to gas chromatography analysis in order to simplify the task of isolation and identification of single components. The oil of the hop (*Humulus lupulus* L. var. Bullion) isolated by the method of Wright and Connery¹ has been fractionated as follows: hydrocarbons were selectively separated from oxygenated compounds through alumina or silica-gel columns using light petroleum ether as eluant². Esters and ketones were separated from alcohols by selective elution from a neutral alumina column using absolute ether as eluant. Esters were subjected to methanolysis using mineral acid as catalyst, and the resulting methyl esters separated from the freed alcohols, as described here. Compounds having a straight chain of seven carbons or more were separated from shorter or branched chain compounds by formation of crystalline adducts with urea in methanol³. Carbonyls were extracted from mixtures containing other oxygenated compounds by the Girard method^{4,5}. Unsaturated compounds were separated from saturated compounds by bromination in carbon tetrachloride⁶. Unsaturated compounds having a conjugated double-bond system were separated from others by the Diels-Alder reaction⁷.

Mishandling of essential oils may result in the destruction of some components and the formation of artefacts. Flash-evaporation of compounds in the injection chambers of gas chromatographs has often led to the pyrolysis of some esters and the dehydration of some terpene-alcohols⁸.

The following hop oil fractions were obtained.

(1) A hydrocarbon fraction representing 70 per cent of the total oil was analysed by gas chromatography and found to contain 21 and possibly 26 compounds. The three largest components isolated and identified