Reaction of Fuming Nitric Acid with Polyethylenes*

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INTRODUCTION

It was long ago elucidated that the normal aging of polyethylenes is a free-radical oxidative attack of atmospheric oxygen upon the resin, usually catalyzed by heat or light.[1] So central is oxygen to the customary aging phenomenon, that laboratory tests assessing the accelerated oxidation of polyethylenes have seldom deviated from the use of oxygen gas or of ozone, its allotropic modification. Yet there are obvious advantages, notably that of precise reaction–temperature control, to be gained from measuring the oxidation of polyethylenes by liquid-phase oxidants.

Polyethylene, being hydrocarbonaceous in nature, is subject to attack by nitric acid, just as are its more simple analogues.[2] Thus Beachell and Nemphos[3] showed that polyethylene was oxidatively degraded by nitric acid. Bobalek et. al.[4] likewise studied the debilitating effect of nitric acid upon polyethylene resin. The aim of our study was to inquire into the mechanistic nature of the reaction of fuming nitric acid with polyethylenes, and to relate its characteristics to the more familiar attack upon the resin by oxygen.

EXPERIMENTAL

The totality of sample involvement, as distinct from mere surface attack, is an immanent problem of the reaction of a liquid reagent, such as fuming nitric acid, with an insoluble solid, such as polyethylene. To minimize this problem, finely ground polyethylenes were used in the study. The oxidative effect upon the resin was assessed by specific viscosity measurements.[5] The results are reported as per cent retention of original viscosity. Table I illustrates the variation of extent of reaction with degree of resin particulation; Marlex 50 was used. In the other experiments herein reported, all resins were used in the arbitrarily selected mesh size of −80 + 100 as obtained by dry-sieve separation of the ground polymer.

The apparatus used is depicted in Figure 1. It consisted of a 1-l.

TABLE I
Fuming Nitric Acid Oxidation of Marlex 50 Resin at
50°C. for 24 Hours
(Effect of particle size on extent of degradation)

Particle size	Specific viscosity
Retained on #40 mesh	0.222
Retained on #60 mesh	0.207
Retained on #100 mesh	0.239
Passing #100 mesh	0.253

Kjeldahl flask resident in a constant-temperature bath.   Within the flask
was stirred the reaction mixture of suspended resin in acid.   At the con-
clusion of the selected reaction time, the flask contents were copiously
quenched with distilled water (to 4 l.), and the resin separated upon a
sintered Buchner funnel.   The resin was water-washed until litmus
paper showed the wash-water to be free of acid.   It was then dried *in vacuo*
at room temperature.   The dried resin was then suitable for molding
operations as required.

A simplification of the reaction kinetics was effected by using so large
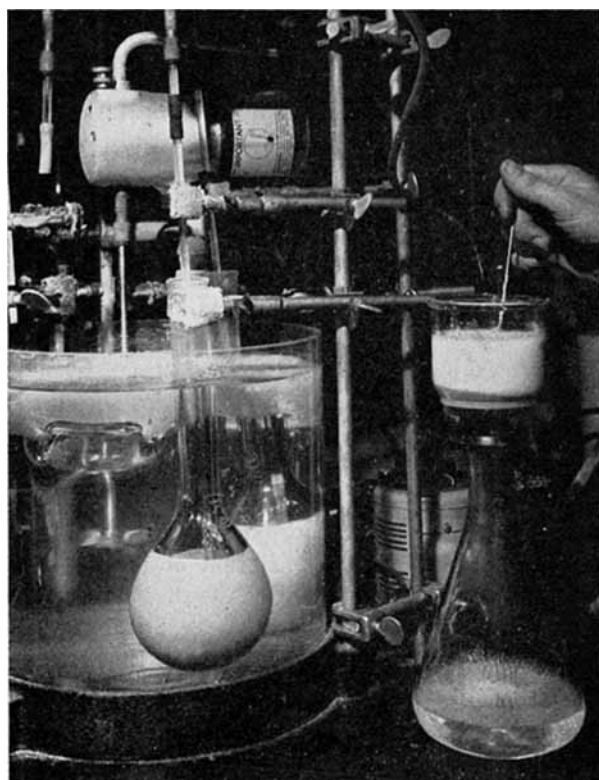an excess of nitric acid as to render its concentration invariant.   Figure

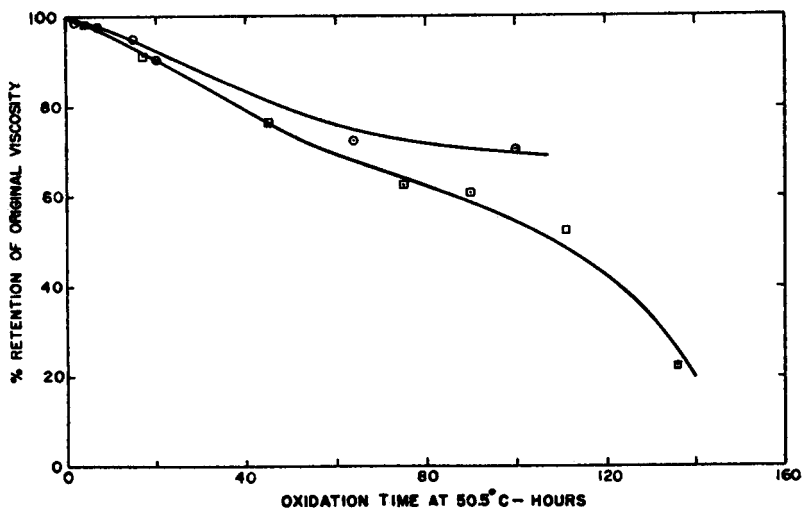Fig. 1. Apparatus used in experiments.

Fig. 2. Fuming nitric acid oxidation of polyethylene resin showing effect of acid/resin ratio: (⊙) 20 g. resin in 100 ml. acid; (□) 75 g. resin in 600 ml. acid.

2 illustrates the influence of the acid-to-resin ratio upon the rate of reaction. In the reported experiments the ratio used was 75 g. resin to 600 ml. fuming nitric acid. That this proportion of reactants provided the necessary excess of oxidant is shown in Figure 3. It is seen that the curve, representing rate of reaction, is reproduced precisely in a second experiment, in which, unlike the first experiment, the nitric acid was replaced by fresh oxidant after 96 hrs. of use.
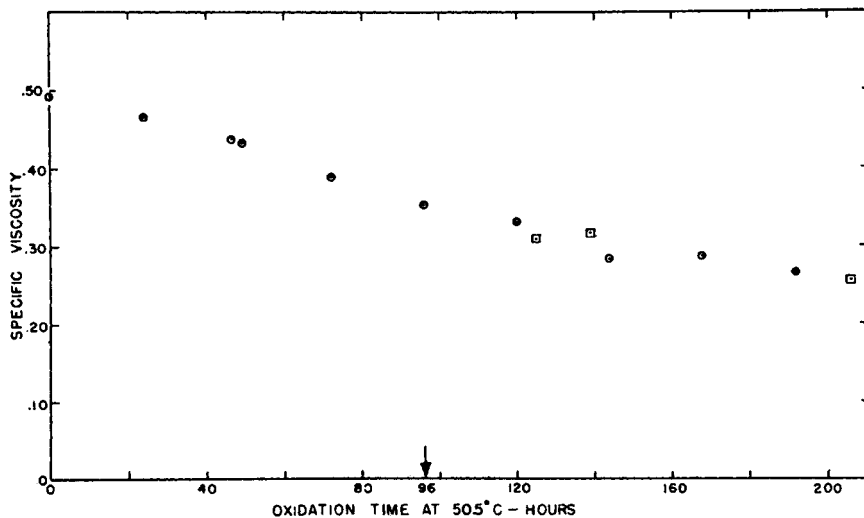

Fig. 3. Effect of fresh acid upon resin degradation: (⊙) Spencer Hi-D resin (straight run); (□) fresh acid added at 96 hrs.

As expected, the rate of reaction was found to be sharply dependent upon temperature; see Figure 4. For a study of the subject reaction over a convenient time interval, a reaction temperature of 50°C. was selected.

The polyethylene resins were obtained directly from their several manufacturers. The grinding of these resins was carried out under liquid nitrogen by the Liquid Nitrogen Processing Corporation of Malvern, Pennsylvania. The fuming nitric acid was Baker's analyzed reagent, 90% assay, sp. gr. 1.50.
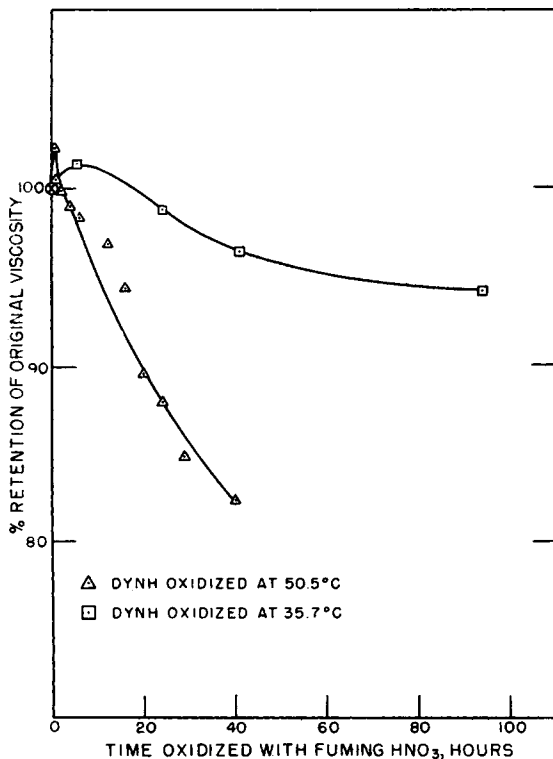

Fig. 4. Nitric acid oxidation of polyethylene resins, showing effect of temperature upon oxidation of DYNH resin: (△) DYNH oxidized at 50.5°C.; (▢) DYNH oxidized at 35.7°C.

COMPARISON WITH OXYGEN REACTION

Hydroperoxide and Carbonyl Groups

Among the molecular innovations that occur during the reaction of polyethylenes with oxygen gas is the appearance of hydroperoxidic and carbonylic functional groups.[6] It is reasoned from the general chemistry of hydrocarbon oxidation that the hyperoxide groups constitute the first oxidative structure formed, and that the carbonyl-containing entities derive from them.[7] It is also known, although the exact chemistry remains

TABLE II
Fuming Nitric Acid Oxidation of Alathon 20 Resin

Hours oxidized at 50.5°C.	Specific viscosity	Carbonyl groups per 2000 C atoms	Peroxide content
0	0.505	0.02	—
2	0.520	0.21	—
7	0.507	0.28	—
16	0.482	0.43	—
23	0.465	0.50	—
41	0.411	0.92	—
65	0.347	1.6	0.14
75	0.263	4.4	0.14
100	0.236	5.6	0.15
140	0.223	6.2	0.17

largely conjectural, that these functional groups are precursors of the polymeric chain-scission reaction which, along with the crosslinking reaction, characterizes the oxidative degradation of polyethylenes.[8]

Beachell and Nemphos[3] have already shown that the reaction of fuming nitric acid with polyethylenes is productive of structures containing these groups. Table II confirms this finding in the case of Alathon 20 resin. Table III gives a similar picture of DYND resin. In neither case is the buildup of hydroperoxide concentration particularly large. This, however, is in accord with the known ephemeral nature of these bodies in the hydrocarbon oxidation scheme.

Crosslinking versus Chain Scission

The two chief consequences to molecular structure of the reaction of polyethylenes with oxygen are the aforementioned concurrent and competitive crosslinking and chain-cutting reactions. In terms of their effect on

TABLE III
Fuming Nitric Acid Oxidation of DYND Resin

Hours oxidized at 50.5°C.	Specific viscosity	Carbonyl groups per 2000 C atoms	Peroxide content
0	0.401	0.0	0.001
2	0.402	0.0	0.073
4	0.398	0.01	0.081
6	0.395	0.0	0.105
16	0.366	0.11	0.105
28	0.354	0.0	0.207
48	0.279	0.0	0.271
72	0.233	0.41	0.577
100	0.170	2.16	0.367
166	0.162	1.76	0.625

specific solution viscosity values, these reactions are antagonistic, since crosslinking aggrandizes chain size while chain scission diminishes it. Figure 5 shows a typical curve of the variance of specific solution viscosity with extent of polyethylene oxidation induced by atmospheric oxygen during hot milling. The maximum in the specific solution viscosity values represents the predominance of crosslinking over chain scission at that point. The subsequent progressive ebb of viscosity values is a resultant of the progressive dominance of chain scission over crosslinking. The opposite effect predominates during the viscosity buildup, to the maximum. This curve is typical of polyethylenes oxidized by oxygen. Solution viscosity curves of polyethylenes oxidized by fuming nitric acid show no such maximum point or, at best, only an attenuated tendency toward
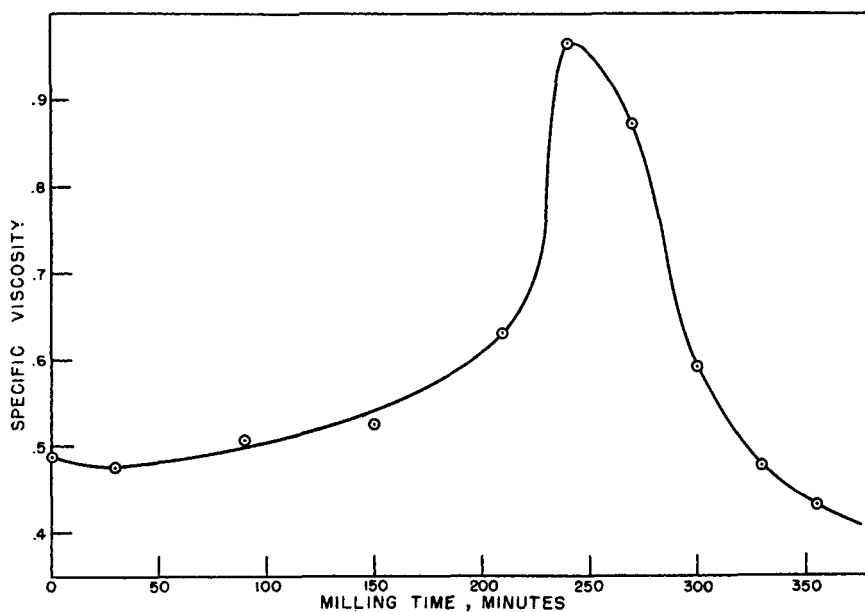

Fig. 5. Variation of solution viscosity with milling time: Alathon 20 at 160°C.

one. The absence of a distinct reaction period during which crosslinking overshadows chain scission may, however, be merely a consequence of the ferocity of the oxidative attack of fuming nitric acid upon polyethylenes. The vigor of the attack could tend to telescope the time during which crosslinking prevails, to a point at which it would go undetected. It is noteworthy in this connection that an incipient hump in the curve does occur for DYNH resin (Union Carbide Polyethylene) at the milder reaction temperature of 35°C., as shown in Figure 4.

Electrical and Flow Properties

Air-oxidized polyethylenes, as a consequence of their acquired polar functional groups, become increasingly better conductors of electricity the

more they are oxidized. That this is also true of polyethylene resins oxidized by fuming nitric acid is illustrated in Table IV, wherein the increase in dissipation factor for resins DYNF and Alathon 10 and 20 is seen to parallel increased exposure of the resins to fuming nitric acid. It is also shown that these same resins undergo a similar increase in dissipation factor upon being air oxidized on a hot mill.

TABLE IV

Development of Changes in Dissipation Factor: Fuming HNO_3 vs. Hot Mill Oxidation

Residence in HNO_3, hr.	Dissipation factor	Mill time, min.	Dissipation factor	Mill time, min.	Dissipation factor
Alathon 10					
0	0.0003	0	0.0002	210	0.0014
17	0.0060	30	0.0002	240	0.0017
45	0.010	60	0.0003	270	0.0020
75	0.0155	90	0.0003	300	0.0025
90	0.0155	120	0.0005	330	0.0030
111	0.0187	150	0.0008	360	0.0032
136	0.0279	180	0.0008	390	0.0037
Alathon 20					
0	0.0005	0	0.0006	240	0.0046
2	0.0028	30	0.0007	270	0.0058
7	0.0035	60	0.0011	300	0.0066
16	0.0051	90	0.0013	330	0.0076
23	0.0061	120	0.0013	355	0.0075
41	0.0088	150	0.0021		
65	0.013	180	0.0028		
75	0.0185	210	0.0039		
100	0.020				
140	0.022				
DYNF					
0	0.0003	0	0.0004	210	0.0024
17	0.0089	30	0.0003	240	0.0030
40	0.013	60	0.0006	270	0.0033
72	0.020	90	0.0011	300	0.0042
90	0.025	120	0.0014	330	0.0043
120	0.027	150	0.0018	360	0.0048
150	0.031	180	0.0021	390	0.0063

It was previously stated that the specific viscosity values of polyethylenes subjected to incremental exposure to fuming nitric acid decreased in response to the progressive fragmentation of the polymer chains. Not surprisingly, therefore, such other flow properties as melt index also exhibited an increase in flow value. The same effect has been reported for zero strength time values of these resins, whether oxidized by air or by fuming nitric acid.[9]

Effect of Methyl Branching

The different positions within an organic molecule which may be occupied by a hydrogen atom are known to influence the ease with which that atom responds to free-radical attack. Except for allylic hydrogens, tertiary hydrogens are probably the most readily affected. It is for this reason that branching and crosslinking add to the predilection of a resin for oxidative attack. The correlation of extent of methyl branching in polyolefins with susceptibility to attack by oxygen gas has been demonstrated.[10] Table V indicates that exactly the same correlation exists between the frequency of methyl branching in a resin and its sensitivity to fuming nitric acid.

TABLE V
Effect of Methyl Branching upon Extent of Oxidation by
Fuming Nitric Acid

Resin	Methyl groups per 1000 C atoms	Retention of specific viscosity after 48 hrs. of oxidation, %
1. Linear polyethylene	1.0	55.4
2. Ethylene–propylene Copolymer	10.7	48.8
3. Ethylene–propylene Copolymer	21.0	47.3
4. Ethylene–propylene Copolymer	35.5	46.4
5. Polypropylene	333.0	12.0

Nitration

The oxidative effect of fuming nitric acid upon polyethylenes is accompanied by the introduction of nitrogen-containing groups into the polymer.[3] Table VI presents this phenomenon as occurring in five polyethylenes and, by inference, as applying generally to all polyethylenes. The data presented also suggest that nitration is not a consequence of temperature of reaction *per se*, but rather a concomitance of the severity or extent of reaction between the resin and oxidant.

UTILITY OF PROCEDURE

Differentiation Among Resins

It has already been demonstrated that polyethylenes differ among themselves in the rate at which they absorb oxygen gas.[10] This is, of course, a consequence of the different structural features, such as bonding, branching, and unsaturation, that characterize the various polyethylenes. It is not surprising, therefore, that polyethylenes also differentiate among

TABLE VI
Analysis for Nitrogen Resins Oxidized with Fuming Nitric
Acid at 50.5°C.

A. Five Different Resins		
Resin	Hours oxidized	N content, %
A	150	0.26
B	140	0.27
C	100	0.20
D	166	0.42
E	140	0.38
B. DYND Polyethylene Oxidized for Varying Times		
	0	0.0
	2	0.20
	4	0.32
	6	0.19
	16	0.36
	28	0.37
	48	0.50
	72	0.49
	100	0.56
	166	0.63

themselves, as is shown in Figure 6, with regard to their reactivity to fuming nitric acid. What is perhaps surprising is that, as is shown in Figure 7, the linear resins exhibit a more severe response to the fuming nitric acid than do conventional polyethylenes.

Measurement of Oxidizability

It is common practice to incorporate antioxidants into polyethylenes in order to immunize the resins against oxidative deterioration during processing or use. The assessment of the amount of antioxidative protection possessed by the polymers is made by measuring the induction period exhibited during exposure to oxygen at elevated temperatures.[10,11] The basis of this assay is the known ability of antioxidants, commonly amines or phenols, to inhibit the uptake of oxygen by the resin. Generally, the larger the quantity of antioxidant, the greater the degree of protection. This relationship need, however, not be linear.[12] In any case, measurement of the time interval to the point of oxygen uptake reflects on the protection conferred upon a resin by the presence of antioxidant, rather than on the oxidizability of the resin itself.

Figure 8 illustrates that Tenite 800 shows the same rate of reaction with fuming nitric acid, whether it is devoid of antioxidative protection or whether it contains 0.05% quantities of di-(1-hydroxy-2-tert-butyl-5-methyl) phenyl sulfide (Santonox) or 0.07% diphenyl paraphenylenediamine. This means that polyethylene oxidation by fuming nitric acid is not influenced by, at least customary quantities of, common antioxidants. This reaction, then, permits the assessment of the inherent
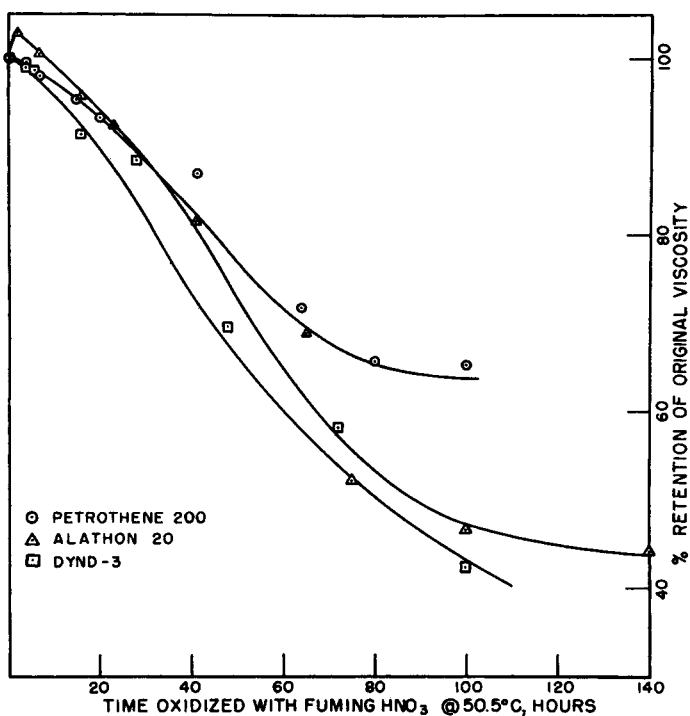
Fig. 6. Nitric acid oxidation of Conventional (low-density) polyethylene resins: (⊙) Petrothene 200; (△) Alathon 20; (□) DYND-3.
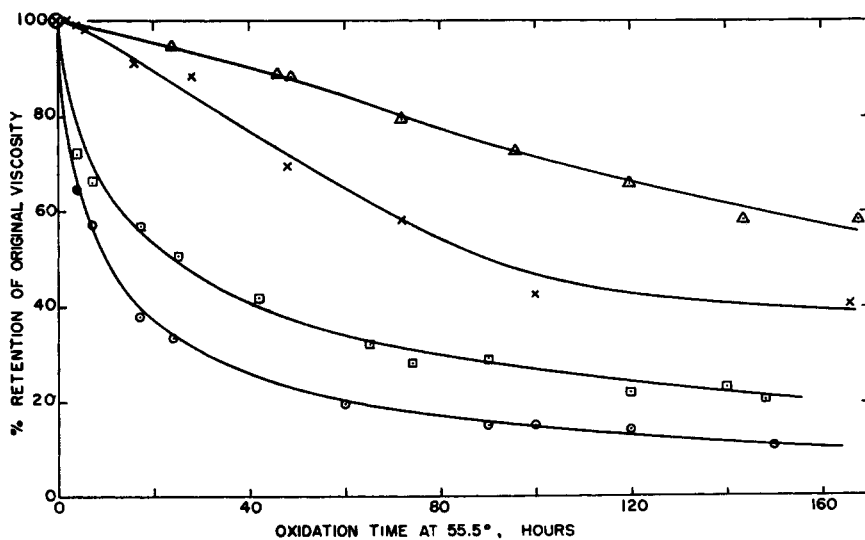

Fig. 7. Fuming nitric acid oxidation curves showing differentiation among polyethylene resins: (⊙) high-density solid-catalyst type; (□) high-density Ziegler type; (△) intermediate density; (✕) conventional low densities.

oxidizability of polyethylenes unencumbered by the interference of anti-oxidative substances whether of willfull on adventitious occurrence.
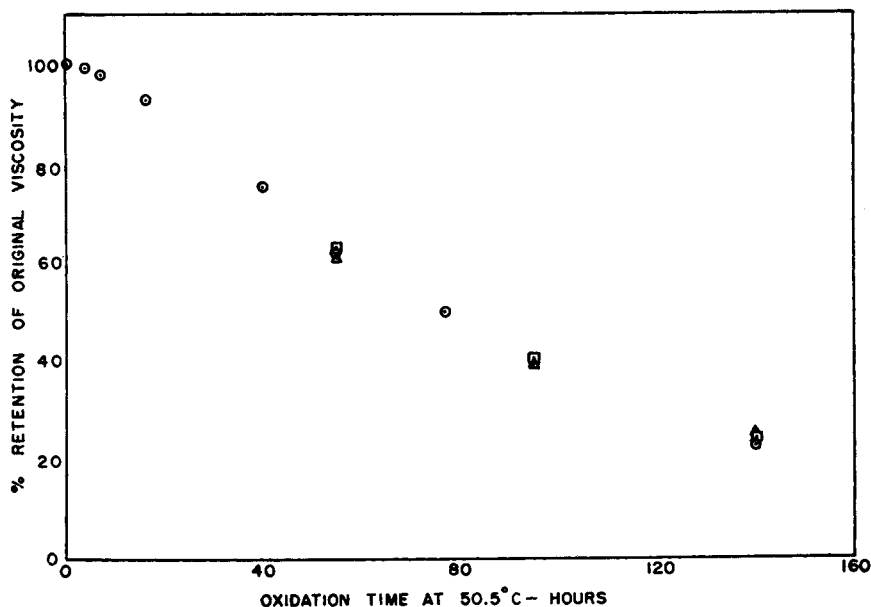
Fig. 8. Fuming nitric acid oxidation of polyethylene resins showing lack of influence of antioxidant on the reaction: (⊙) Tenite 800, no antioxidant; (△) Tenite 800, 0.05% phenolic; (□) Tenite 800, 0.07% amine.

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Synopsis

    The oxidative effect of fuming nitric acid upon finely ground polyethylenes is observed by plotting changes in specific solution viscosity values against duration of reaction. The similarity in relationship between this reaction and that of polyethylenes with oxygen is set forth.   It is shown that this reaction, like that between polyethylenes and oxygen gas, produces hydroperoxide and carbonyl structures, and results largely in scission of the polymeric chains.   The effect of these oxidative alterations in decreasing the electrical resistivity and in increasing the flow properties of the subject resins is illustrated.   The identical influence of methyl branching in favoring the reaction of polyethylenes with both oxygen and with fuming nitric acid is demonstrated.   Nitration is seen to be a consequence of extent of reaction rather than of reaction temperature itself.   The utility of this reaction in differentiating among polyethylenes is indicated. In this regard it is seen that the linear polymers are more severely affected by fuming nitric acid than are conventional polyethylenes.   Finally, the usefulness of this reaction in assessing the inherent oxidizability of polyethylene resins, independent of the presence or absence of antioxidants, is proposed.

Résumé

    On observe l'oxydation par l'acide nitrique fumant des polyéthylènes finement broyés, en mettant en diagramme les variations de la viscosité spécifique de la solution en fonction du temps de réaction.   On montre la similitude de relation entre cette réaction et la réaction des polyéthylènes avec l'oxygène.   On montre que cette réaction, comme celle entre les polyéthylènes et l'oxygène gazeux, produit des structures hydroperoxydiques et carbonyliques et provoque de nombreuses ruptures de la chaîne polymérique.   On explique les effets de ces oxydations, sur la diminution de résistivité électrique et sur l'augmentation des propriétés d'écoulement de la résine traitée.   On démontre l'influence identique de l'addition d'un groupe méthyle, sur la réaction du polyéthylène tant avec l'oxygène qu'avec l'acide nitrique fumant.   La nitration semble être une conséquence de l'étendue de la réaction plutôt que de la température de réaction elle-même.   On montre l'utilité de cette réaction pour la différentation des polyéthylènes. A ce point de vue, on voit que le polymères linéaires sont plus souvent attaqués par l'acide nitrique fumant que les polyéthylènes conventionnels.   En conclusion, on propose l'emploi de cette réaction pour l'évaluation de l'oxydabilité inhérente des résines de pooyéthylène, indépendamment de la présence ou de l'absence d'antioxydants.

Zusammenfassung

    Die oxydierende Wirkung von rauchender Salpetersäure auf fein gemahlenes Polyäthylen wird anhand einer Auftragung der spezifischen Viskosität der Lösung gegen die Reaktionsdauer festgestellt.   Die Ähnlichkeit der Beziehungen für diese Reaktion und für die Reaktion von Polyäthylen mit Sauerstoff wird dargelegt.   Es wird gezeigt, dass bei dieser Reaktion, sowie bei der zwischen Polyäthylen und Sauerstoffgas, Hydroperoxyde und Carbonylstrukturen entstehen und eine weitgehende Spaltung der Polymerketten eintritt.   Der Einfluss dieser Veränderungen auf die Herabsetzung des elek-

trischen Widerstands und auf die Erhöhung der Fliessfähigkeit der behandelten Harze wird gezeigt. Methylverzweigung besitzt einen identischen, begünstigenden Einfluss auf die Reaktion von Polyäthylen mit Sauerstoff und mit rauchender Salpetersäure. Die Nitrierung erweist sich mehr als eine Folge des Ausmasses der Reaktion, als der Reaktionstemperatur selbst. Die Brauchbarkeit dieser Reaktion zur Unterscheidung von Polyäthylenen wird gezeigt. In dieser Hinsicht ergibt sich eine tiefergreifende Einwirkung von rauchender Salpetersäure auf lineare Polymere als auf die konventionellen Polyäthylene. Schliesslich wird diese Reaktion als geeignet zur Beurteilung der spezifischen Oxydierbarkeit von Polyäthylenharzen, unabhängig von der Gegenwart oder Abwesenheit von Antioxydantien, empfohlen.