

BACTERICIDAL NONIONIC DETERGENTS

H. J. FERLIN AND J. V. KARABINOS
Blockson Chemical Company, Joliet

As reported in a previous publication,¹ the condensation product of tall oil and ethylene oxide (polyethenoxy tallate) was treated with ozone and pronounced bactericidal activity of the ozonide was noted. In conjunction with this problem, it was found that the corresponding oleic ester also showed germicidal activity. The active principle responsible for this phenomenon was thought to be pelargonic acid, an oxidation product of oleic acid. It was later found that other fatty acids in the C₉ to C₁₂ range possess bactericidal activity which was markedly accentuated by increasing acidity.²

This study is concerned with a closer scrutiny of the nature of the bactericidal activity of ozonized nonionic detergents from tall oil to determine whether the activity is due to the pelargonic acid alone, or whether ozone itself, the ozonide, or some other factor plays a role.

EXPERIMENTAL

Preparation of materials. — The polyethenoxy tallate, abietate, and oleate were prepared by condensation of one part by weight of the respective acid with two parts by weight of ethylene oxide gas using the method described in the preceding paper.³

Twenty grams of nonionic detergent was weighed in a tared apparatus suitable for the quantitative adsorption of ozone. The ozone gas was generated in the previously described apparatus¹ and passed into the polyethenoxy ester until no increase in weight was noted, usually about 15 to 20 hours. The percentage of ozone taken up by each 20-gram sample of detergent is shown in table 1 with the number of oxygen atoms for each unsaturated group.

Bacteriological procedure. — The bacteriological procedure is essentially the same as that outlined in a previous paper.¹ However, for purposes of accuracy and uniformity, one modification was made—a 0.2 ml. portion of a 24-hour culture of *Staphylococcus aureus* A.T.C.C. No. 6538, instead of the customary 0.1 ml., was used. This was done primarily to afford a wide range of dilutions with a minimum number of tubes, so that a given sample of the ozonide could be used without permitting any dilution to stand while another group of dilutions was being tested. This was done because of the instability of the ozonide, especially during the time immediately following the ozonization. The activity of a 1:100 dilution dropped off as much within 24 hours as the undiluted ozonide did in over 3 weeks.

The results obtained with each of the polyethenoxy ozonides are shown in figure 1.

¹ H. J. Ferlin, A. T. Ballun, and J. V. Karabinos, *Jour. Am. Oil Chem. Soc.*, 31, 103 (1954).

² J. V. Karabinos and H. J. Ferlin, *Jour. Am. Oil Chem. Soc.*, 31, 228 (1954).

³ A. T. Ballun, G. E. Bartels, and J. V. Karabinos, *Trans. Ill. Acad. Sci.*, vol. 47 (1955).

TABLE 1.—OZONIDES OF POLYETHENOXY ESTERS.

Polyethenoxy ester	% ozone taken up by weight	No. unsaturations (calc'd.)	No. oxygen atoms per mole of ester	No. oxygen atoms per unsaturation
Tallate.....	10.7	1.7	5.9	3.5
Abietate.....	7.3	2.0	4.5	2.2
Oleate.....	7.5	1.0	4.3	4.3

DISCUSSION OF RESULTS

From table 1 it should be noted that the oleate and tallate absorbed more than 3 atoms of oxygen for each unsaturated linkage as prescribed by theory while the abietate took up somewhat less weight. From figure 1 it is to be noted that the aliphatic ozonides (A and B) possess a large initial bactericidal activity which falls off rapidly to an activity in the neighborhood of pel-

argonic acid itself. This initial activity is, however, not shown by the polyethenoxy abietate ozonide (C). It would seem therefore that this initial activity is not due to the simple addition of ozone to all unsaturated linkages, nor to pelargonic acid alone. It was noted also that polyethenoxy oleate did not lose weight upon standing; thus, the initial activity could not have been due to the liberation of nascent oxygen by these aliphatic ozonides. To determine whether the polyethenoxy group plays any role in the bactericidal activity, oleic acid was ozonized and absorbed 4 atoms of oxygen. The initial activity was found to be very high with the highest dilution giving negative growth being about 1:85,000. This activity dropped off rapidly upon standing. It seemed that the initial activity was tied up in some way with the ozonization of aliphatic carbon to carbon double bonds and had little to do with the detergents themselves. From table 1 it appears that the "ozonides" of the oleate or tallate take up more than the 3 atoms of oxygen as required by theory for an ozonide (I) and may be in the neighborhood of 4 atoms of oxygen for each unsaturation. A peroxide formula such as (II) would answer these requirements.

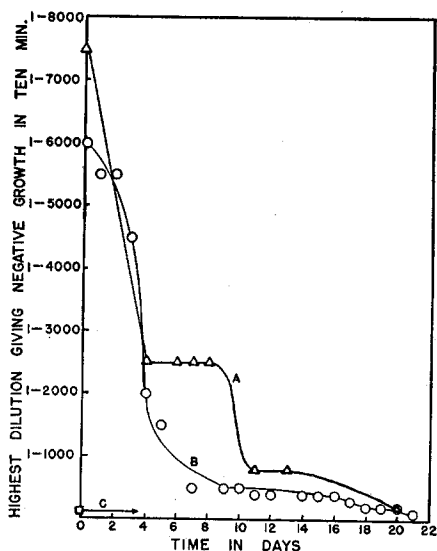
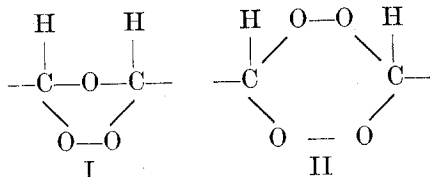


FIG. 1.—Loss of bactericidal activity with time of ozonized polyethenoxy detergents prepared from: A, oleic acid; B, tall oil; and C, abietic acid.



It may be that a peroxide formula such as II, upon standing, slowly rearranges to the corresponding acids such as pelargonic and azelaic, in the case of oleic acid. Further experi-

ments are underway to determine the nature of this bactericidal activity of various ozonides of aliphatic and alicyclic olefin compounds. It would appear that only a small part of the activity of polyethenoxy tallate or oleate ozonides is actually due to the pelargonic acid itself, and that the initial germicidal activity is apparently due to some peculiarity in the structure of the "ozonide" such as represented by II.