TABLE IV

Properties of Films from the Unsaturated Esters

Ester	C_2H_4O groups per AGU	After 72 hr drying time	
		Type of film	Water test[a]
Dilinolenate	16	Slightly tacky	Failed
Dilinolenate	20	Tacky; soft	Failed
Dilinseedate	15	Slightly tacky	Good
Dilinseedate	20	Tacky	Good
Linseedate	20	Slightly tacky	Good

[a] Good, no apparent change in film; failed, film washed off but did not dissolve.

of an ethylene glycol glycoside containing 20 mole equivalents of ethylene oxide. No additional catalyst was added since there was sufficient alkaline catalyst in the polyether from the etherification reaction. The reactants were heated under nitrogen with stirring at 150C for 1.75 hr, during which time a solution was formed. The solution was then slowly heated to 260C for 45 min (2). Properties of this linseedate are listed in Table III.

Physical Characteristics of the Esters

Emulsifying Properties. Forty milliliters of 0.1% aqueous solution of the polyether esters were mixed with 40 ml of light paraffin oil, N.F., in a 500-ml glass-stoppered Erlenmeyer flask and manually shaken in five cycles. Each cycle consisted of five violent downward motions and 1 min of standing. The emulsion was then poured into a 100-ml graduate cylinder, and the time required for 10 ml of the aqueous phase to separate was recorded (10). Values for these esters, reported in Table III, are comparable to those reported for methyl glucoside polyether esters (7).

Film-Forming Properties. Polyether unsaturated esters (3 g) were mixed with enough naphthenate drier to give a mixture containing 0.42% lead and 0.042% cobalt. The esters were then drawn into films with a doctor blade at a wet thickness of 0.005 in. on glass plates. After drying 72 hr at room temperature, the films were characterized as reported in Table IV. An additional 48 hr of drying did not appreciably change film properties. A "water test" was made by allowing 5.2 liters of water, at 27C, to run from a spigot onto the films (8). The water-soluble esters, which form relatively insoluble films upon drying, have potential utility as emulsifiers in water-base paints.

ACKNOWLEDGMENTS

Assistance with synthesis and analysis by Bonnie L. Wade and hydroxyl analysis by Clara E. McGrew.

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[Received May 7, 1962—Accepted November 10, 1962]

A Study of the Biodegradation of Anionic Synthetic Detergents

A New Laboratory Test

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Abstract

The biodegradation of anionic synthetic detergents is studied by means of a new laboratory test. The bacterial source used in this test is activated sludge from the Sewage Works at Amsterdam. Important differences in biological "softness" were found between various detergents with this test, which gives results similar to those found in pilot plant experiments.

Introduction

MANY PUBLICATIONS, especially from the United Kingdom, have dealt with troublesome foam in Sewage Works and rivers which is caused by the presence of non-degraded anionic synthetic detergents in effluent.

From the work done so far it is clear that a certain type of synthetic detergent viz. the alkylbenzene sulfonate based on propylene tetramer (DOBS PT) is the main offender because the heavily branched structure of this product is attacked more slowly and to a lesser extent by the bacteria in the Sewage purification process than e.g., primary alcohol sulfates or other synthetic detergents with straighter chains.

In this laboratory the biodegradation of syndets has been studied by means of a test using water from the river IJ as the source of bacteria for the degradation and also by means of activated-sludge pilot-plant experiments (1).

The river-water test, which can be considered representative for biodegradation of anionic detergents in open water, is carried out by making a solution of the anionic detergent in the water and storing this solution without aeration. The amount of detergent degraded by the bacteria present in the water is determined at suitable intervals by the method of Longwell and Maniece (2,3,4).

As the IJ-water test gives a very slow degradation we set out to develop a laboratory test which was likely to provide conditions nearer to those prevailing in actual Sewage Works.

Description of the Test

To a solution of various inorganic salts in distilled water activated sludge from the Sewage Works in Amsterdam and a small amount (10 ppm) of an anionic detergent are added. The mixture is aerated at room temp. Every day homogeneous samples containing the activated sludge are taken from the test liquor and the amount of detergent left is determined according to the method of Longwell and Maniece. The test lasts for seven days after which in general the ultimate hard residue is reached. As activated sludge usually contains material that interferes in the determination of the amount of detergent, this must first be removed. For this purpose the activated sludge suspension is washed with distilled water by centrifugation, resuspended, and aerated before use.

In order to ensure constancy of the bioactivity of the activated sludge it is stored at 0C. In this way the sludge retains about the same activity for several months. The test described has been used successfully in our laboratory for about a year.

Experimental Procedure

Reagents

Alkaline Phosphate Solution—10 g of AR[1] anhydrous Na_2HPO_4 is dissolved in distilled water. The pH is adjusted to 10 by adding NaOH and the volume made up to 1 liter with distilled water.

Neutral Methylene Blue Solutionn—0.35 g of methylene blue is dissolved in 1 liter of distilled water.[2]

Acid Methylene Blue Solution—0.35 g methylene blue is dissolved in 500 ml of distilled water, 6.5 ml of AR sulfuric acid (100%; sp.gr. 1.84) is added and the volume made up to 1 liter with distilled water.

Chloroform AR

Activated Sludge Suspension—A fresh activated sludge suspension (containing approx 1% evaporation residue) from a sewage purification plant. This suspension has to be stored at 0C.

Salt Solution—This contains the following salts in the specified quantities:

0.1 ppm $FeCl_3 \cdot 6H_2O$
27 ppm $CaCl_2$
25 ppm $MgSO_4 \cdot 7H_2O$
2 ppm $(NH_4)_2SO_4$

It further contains 0.125% of a phosphate buffer prepared by dissolving 3.4 g of AR KH_2PO_4 in 50 ml distilled water, adding approx 17.5 ml of I N NaOH solution until pH 7.2, and making up to 100 ml.

Procedure

Washing Out of Sludge Suspension—Four centrifuge tubes of 250 ml are filled each with 25 ml of the homogeneous activated sludge suspension. They are centrifuged for 15 min at 2600 rpm and the upper layer (water) is rejected. The remaining solid material is thoroughly mixed with 150 ml distilled water and again centrifuged. This process is repeated 10 times. The solid material from each tube is then suspended separately in an amount of the salt solution so as to make up the original volume. This suspension is placed in a 500 ml gas washing bottle with a sintered glass filter (Schott & Gen. Mainz, G3 porosity) and aerated for 16 hr at an aeration rate of about 1 liter/hr and at room temp.

Degradation—To the 25 ml of purified activated sludge suspension from one centrifuge tube 470 ml of the salt solution and 5 ml of an aqueous solution of the detergent under test containing 1000 ppm of active material are added. 300 ml of this mixture is placed in a 500 ml gas-washing bottle and air, saturated with water vapor, is bubbled through the solution at a rate of 1 liter/hr and at room temp. Every day, a 10-ml homogeneous sample is taken and placed in a separatory funnel containing 90 ml of distilled water, 10 ml of alkaline phosphate solution, 5 ml of neutral methylene blue solution and 50 ml of chloroform. The solution is shaken for 1 min and the chloroform layer (with possible emulsion) is run into the second separatory funnel, which contains 110 ml of distilled water and 5 ml of acid methylene blue solution. After shaking for 1 min the chloroform layer is filtered through a plug of absorbent cotton. A volume sufficient for aborbance measurement of the methylene blue/active material complex at 650 mμ is collected, the first 5 ml of filtrate being rejected. Any sensitive photoelectric colorimeter, equipped either with a monochromatic light source or a suitable filter (Ilford No. 607 orange) can be used.

Calculation—The percentage surface-active material left in the sample can be calculated by means of the following equation:

$$\% \text{ active material left} = \frac{100\,(D - B_d)}{A - B_o}$$

where: A = absorbance at the start of the test
B_o = ditto of blank
D = absorbance after d days of degradation
B_d = ditto of blank

Tests are best run in duplicate, and blank values must be determined and suitably allowed for. The repeatability of the results is approx 3%. No differences in bioactivity could be observed between samples of activated sludge taken at different times in the sewage purification plant.

Experimental Results

Among other products the following four have been investigated:

1. Sulfonated "DOBANE" PT[3] (DOBS PT).
2. Sulfonated "DOBANE" JN.[4] The sulfonated product (DOBS JN) is considered as a biologically soft detergent.
3. Sulfonated improved "DOBANE" JN[5] (Improved DOBS JN).
4. Lauryl sulfate.

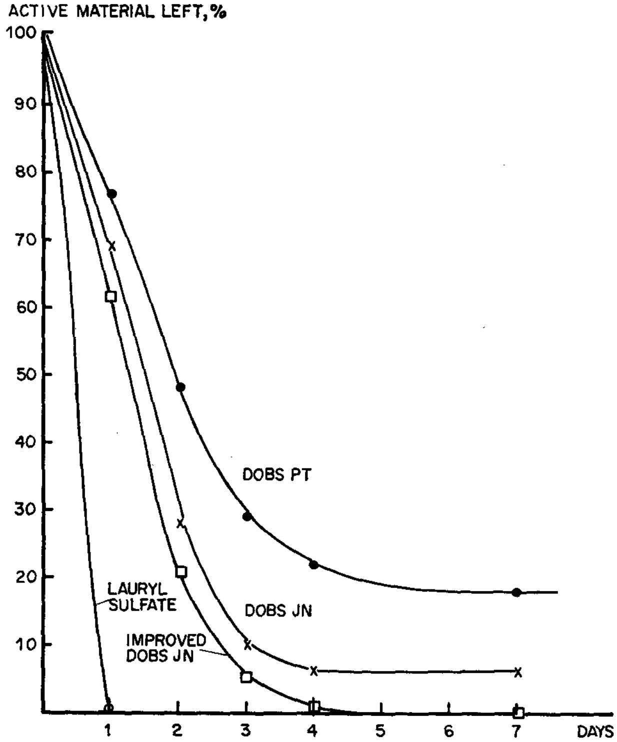

Fig. 1. Biodegradation of four anionic detergents as a function of time.

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[1] AR = Analytical Reagent quality.

[2] The quality of the methylene blue is of importance. In our tests the dye furnished by British Drug Houses Ltd. gave satisfactory results.

[3] An alkylbenzene manufactured by Shell from olefin ex propylene tetramer.

[4] Do. from cracked olefins.

[5] Do. from a predominantly straight-chain olefinic feedstock.

TABLE I

Results of Activated-Sludge Test[a]

Days of degradation	Percentage of active material left			
	DOBS PT	DOBS JN	Improved DOBS JN	Lauryl sulfate
0	100	100	100	100
1	77	69	62	0
2	48	28	21	0
3	29	10	5	0
4	22	6	1	0
7	18	6	0–1	0

[a] Initial detergent concentration 10 ppm, room temp, aeration: 1.0 l/h per 300 cm³.

The results obtained are tabulated in Table I. (See also Fig. 1.)

The differences of the various detergents as to their biological "softness" can be expressed as the "hard-residue ratio." This ratio is given by 100 a/b, where a represents the percentage of test detergent left after seven days and b the percentage of DOBS PT left after the same period. Table II gives the hard residue ratio for the detergents investigated.

From the figures given in Table I and Table II it can be seen that DOBS JN derived from cracked olefins has a much higher hard-residue ratio than the improved DOBS JN prepared from straight-chain olefins or than lauryl sulfate, which is a primary alkyl sulfate.

TABLE II

Hard-Residue Ratio of Various Detergents

Detergent	Hard-residue ratio after 7 days
DOBS JN	33
Improved DOBS JN	0–6
Lauryl sulfate	0
DOBS PT (ref.)	100

The hard-residue ratio for DOBS JN found in this test agrees with the corresponding ratio in pilot plant experiments (approx 30) thus confirming the validity of the new method.

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[Received May 7, 1962—Accepted November 5, 1962]

• *Letter to the Editor*

A Quick Method of Detecting Castor Oil in Vegetable Oils

IN THE COURSE of other investigations I have found that if a solution of molybdic acid is added to petroleum ether solution of an oil sample, a heavy turbidity immediately develops in the solution if the sample contains castor oil. This possible test may be of interest to detect addition of castor oil to other oils.

In order to carry out the test the following procedure was used.

Reagents Required. (a) Petroleum ether (B.P. 40–60C) acidified with 2% (by volume) analytical grade concd hydrochloric acid. (b) [2]A concentrated sulphuric acid solution of molybdic acid containing 1.25 g of ammonium molybdate/100 ml of analytical reagent (s.p. gr 1.84).

Procedure. Dissolve one ml of the filtered oil sample in 10 ml of the reagent (a)—acidified petroleum ether, in a clean and dry test tube. Shake it vigorously. Add to it a drop of the reagent (b). If castor oil is present in the sample, even up to 2%, a strong turbidity immediately develops. Whereas in the case of other pure oils the addition of the reagent (b) causes no turbidity and the solution remains perfectly clear and transparent.

It is important to notice that turbidity is to be examined immediately after addition of the reagent, preferably against a source of light, because otherwise the oil present in the solution may get charred by sulphuric acid and may become hazy. In addition to this it is also important that the final observation in the test-tube should be seen within 15 sec, as concd sulphuric acid starts charring the oil very quickly.

It was also observed that the addition of hydrochloric acid in petroleum ether is essential, because otherwise certain oils like sesame and mahwa (Bassia) are immediately affected with sulphuric acid and become black. The presence of hydrochloric acid in petroleum ether seems to retard discoloring effects also.

The behavior of various vegetable oils, pure as well as adulterated with 2% castor oil, is as follows:

S. No.	Oils	Observations
1	a) Peanut oil b) With 2% castor oil	Solution remains clear Solution immediately became turbid
2	a) Cottonseed oil b) With 2% castor oil	Slightly brownish but clear Light green turbidity
3	a) Sesame oil b) With 2% castor oil	Darkish green and clear Whitish dirty green turbidity
4	a) Mahwa oil b) With 2% castor oil	Blackish brown and clear Whitish brown turbidity
5	a) Soybean oil b) With 2% castor oil	Light blue and clear Bluish white turbidity
6	a) Corn oil b) With 2% castor oil	Brown and clear. Dark brown turbidity
7	a) Mustard oil b) With 2% castor oil	Clear Gray turbidity
8	a) Linseed oil b) With 2% castor oil	Light brown and clear Light brown turbidity

Note—The only exception in this test is poppy-seed oil, which gives turbidity even in pure state.

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[Received July 31, 1962]

• *Erratum*

JAOCS, *39*, page 454, October, 1962, (also see Errata, JAOCS, *40*, page 40, January, 1963). RHEINECK ET AL.: CHEMISTRY AND TECHNOLOGY OF SOME DRYING OIL FATTY ACID ESTERS OF POLYVINYL ALCOHOL. Under the sub-heading "Use of Other Solvents:"

For polyvinyl alcohol this is:

M = molecular weight per unit, 44
d = density, $\underline{1.21}$
CH_2 = 133
CH = 28
OH = $\underline{170}$
ΣG = 331