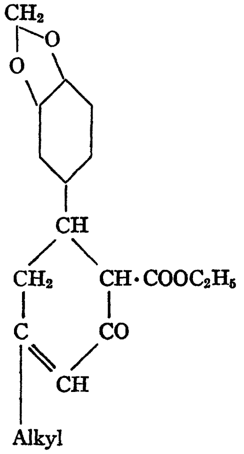
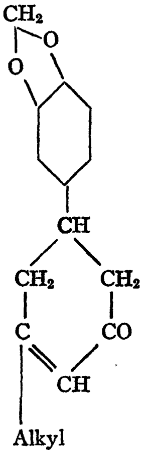
from the fact that a solution of 300 mg. of this substance in combination with 30 mg. of pyrethrins in 100 cc. of odorless base oil gave 99 per cent knockdown and 90 per cent kill of houseflies when tested according to the Peet-Grady method (*8*); 30 mg. of pyrethrins dissolved in 100 cc. of odorless base oil will give a knockdown of a little better than 80 per cent and a kill of about 15 per cent; 300 mg. of the condensation product dissolved in 100 cc. of odorless base oil will, under the test conditions, give a knockdown of less than 10 per cent and therefore practically no kill.

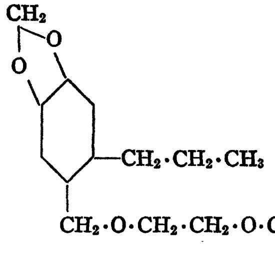
The technical reaction product found prompt commercial acceptance under the name "piperonyl cyclohexenone." It was subsequently found (*6*) to contain 80 per cent of a mixture of





in addition to higher molecular condensation products.

Although the physical characteristics of "piperonyl cyclohexenone" made it satisfactory enough to be useful in insecticidal sprays in conjunction with secondary solvents, the search was intensified for a product of increased activity and of complete miscibility with freon and with petroleum hydrocarbons. (3,4-Methylene-dioxy-6-propyl benzyl) (butyl) diethylene-glycol ether



was synthetized in this laboratory (*7*) and found to possess the desired properties. This also shared with the pyrethrins the property of being practically nontoxic to warm-blooded animals (M.L.D.: 7.5 grams/kg.). The product boils at 180° at 1 mm. It is a colorless liquid, soluble in all the common organic solvents.

The activity of piperonyl butoxide (the name given the technical product containing 80 per cent of pure compound) is indicated in Table 1. The tests were run according to the established Peet-Grady procedure (*8*) by dissolving the indicated quantities of piperonyl butoxide and pyrethrins in 100 cc. of odorless base oil.

While it is apparent that we still have no substitute available for pyrethrins, it is now possible to employ the latter in a very much lower concentration and to obtain effectiveness which would be uneconomical, if at all feasible, if pure pyrethrins were used. It is gratifying that the addition of the synergist does not introduce toxicological hazards.

TABLE 1

Pyrethrins (mg.)	Piperonyl butoxide (mg.)	Knockdown	Kill
20	100	93	62
20	200	96	77
20	400	97	84
30	100	95	59
30	200	97	77
30	400	99	92
40	100	97	74
40	200	98	82
40	400	97	90
40	0	84	34
100	0	95	46
0	300	8	—

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Specific Surfaces of Bone, Apatite, Enamel, and Dentine

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Recently a few preliminary measurements were made of the specific surfaces of some tooth and bone samples and of a synthetic hydroxylapatite.[2] In making the determination, small samples of the four powders were weighed in sample bulbs and the bulbs sealed into the vacuum system. The whole teeth were washed with distilled water and acetone and sealed in bulbs on the apparatus. The system was evacuated to approximately zero pressure and the samples heated for about two hours at 200° C. to drive off any condensed moisture or gases. After this initial operation, the adsorption determination was carried out to obtain several points on the iso-

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[1] Present address: Hydrocarbon Research, Inc., Trenton, New Jersey.

[2] The apatite was prepared in this laboratory (*3*). The bone was glycol-ashed rabbit bone (*2*). The dentine and enamel were samples from human teeth prepared in the powdered form by the Manly-Hodge method (*4*).

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therm curve. Exact details of the procedure cannot be enumerated, but many detailed procedures of gas adsorption methods are described in the literature (*1*).

The results of the tests are given in Table 1. It was impossible to obtain exact values for the whole teeth because not a single equilibrium pressure-volume point necessary for the isotherm could be obtained during a continuous 8-hour determination. The most probable reason for the failure to obtain equilibrium points was the unusually large size of the samples.

TABLE 1

Sample	Approximate particle size	Wt. of sample (grams)	Total surface (sq. cm.)	Specific surface (sq. m./gram)
Apatite		0.0098	5,002	51.1
Dentine	60 mesh	0.0192	461.7	2.4
Enamel	60 "	0.0196	352.8	1.8
Bone ash	60 "	0.0089	8,835	99.3
Tooth #2		1.2845	22,000*	1.77*
Tooth #3		1.0528	16,700*	1.59*

* Estimation.

The surface area results on the powders are amazing. For example, bone ash has about 100 sq. m. of surface/gram. The variation of specific surface between bone, apatite, dentine, and enamel is of special interest because these were of the same particle size (*i.e.* 60 mesh). Presumably these variations revealed differences in the sizes of the submicroscopic crystals of hydroxylapatite.

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Increasing the Spreading Coefficient of Mustard Gas[1]

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It is a well-known fact that small amounts of so-called "capillary active agents," when added to water, greatly reduce the surface tension of that liquid. As a result of this phenomenon, it was assumed that the addition of a low percentage of an appropriate soluble wetting agent to mustard gas (hereafter referred to as H) would reduce its surface tension to such an extent that the interfacial tension between it and water would be reduced sufficiently to increase the spreading coefficient beyond its normal value of 1 to 4.[2] To this end, several of the commercially available wetting agents were tried. Unfortunately, however, most of these, due to their high polarity, were insoluble in H and consequently, in this investigation, Alkaterge-O[3] was used throughout in order to establish the validity of the initial premise. The mustard gas was prepared from thiodiglycol and hydrochloric acid (m.p., 14.25°; purity, 99.5%). Distilled water having a surface tension of 72.0 dynes at 26° was used.

The mathematical reasoning involved in the theory of the spreading of liquids is adequately covered in textbooks on physical chemistry (*1*).

Procedure

All measurements were made by means of the Du Nuoy interfacial tensiometer. All equipment, including the ring, was carefully cleaned in chromic acid. The ring was heated in a Bunsen flame before insertion into its seat in the apparatus. No attempt was made to control the temperature to an accuracy greater than ±1°, since the aim was to find tension differences far greater than those encountered over a 1° range in temperature. Readings were taken at room temperature of about 24°–26°. The results, averaging from about 6 to 8 separate readings, are compiled in Table 1.

TABLE 1

Surface and Interfacial Tensions of H, the System H-H_2O With and Without Alkaterge-O, and the Spreading Coefficient of H Calculated From These Values*

System	Alkaterge-O (%)	Surface tension in air, γ (dynes/cm.)	Interfacial tension (γ AB, dynes/cm.)†	Calculated spreading coefficient of H on water (γB-γA-γAB)
H_2O	0	72.0	—	—
H	0	40.6	23.0‡	+8.4§
H	½	33.2	about 6.0	+32.9
H	1	31.7	" 1.0	+39.3
H	2	31.6	" 1.0 max.	+39.4
H	5	31.4	" 1.0 max.	+39.6

* All values are corrected by means of calibration curve.

† A = surface tension of H; B = surface tension of H_2O; AB = interfacial tension of the system H-H_2O.

‡ A value of 28.4 dynes/cm. at a lower temperature is on record in an Edgewood Arsenal report.

§ A value of + 1.6 has been previously recorded for a lower temperature in an Edgewood Arsenal report.

It is apparent from the data presented that the surface and interfacial tensions of H can be lowered through the addition of 1 per cent of a surface active agent such as Alkaterge-O. The lowering of the tensions is sufficient to increase the spreading coefficient considerably above the value obtained with untreated H.

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[1] Published with the permission of the Chief, Chemical Corps.

[2] Taken from reports on file at Edgewood Arsenal.

[3] An amine of high molecular weight, obtainable from the Commercial Solvents Corporation, New York City. According to the analysis performed in the Edgewood Laboratories, the empirical formula is $C_{22}H_{38}O_2NH_2$.