

Effectiveness of Detergent Solutions

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Abstract

A laboratory method was developed to evaluate quantitatively the effectiveness of various detergent solutions in the removal of different types of soil from flat glass surfaces. The influence of temperature and detergent concentration on the cleaning process was studied.

Introduction

THE PURPOSE of this study was to develop a quantitative method for the comparative evaluation of the cleansing effectiveness of various detergent compounds used in bottle washing on an industrial scale. The only means of evaluating such compounds until now has been in actual plant operation. This is expensive and it is generally difficult to interpret the results meaningfully because of lack of adequate control over important variables. Of these, the quantity and the nature of the soiling material, which is of primary importance, is completely beyond the control of the experimenter. In addition, in such plant tests it is extremely difficult to express any results in truly quantitative terms.

To overcome these problems the authors had to develop:

- 1) standard soils believed to be typical for contaminants encountered in the beverage industry which could be applied in a reproducible way on glass surfaces;
- 2) a method to treat the soiled glass with the detergent to be tested under carefully controlled and reproducible conditions;
- 3) a method to measure accurately the amount of soil before and after treatment of the glass with the detergent to be tested.

Experimental

Soils. Three standard soils were developed: a fat type, a protein type, and a soot type soil. They proved to be reproducible in characteristics, easily applicable on glass surfaces without flaking, nearly insoluble in water, and generally similar to soils encountered in industrial bottle washing. The soot type soil was composed to imitate the soiled bottles being returned from smoky greasy heavy industry establishments such as coal mines, foundries, etc. All soils contained a soft drink syrup consisting of 55% sugar, caramel, 0.2% phosphoric acid, and flavoring extracts. To the fat and protein type soils a stabilizer solution had to be added to prevent a separation of soil components. It consisted of a saturated solution of gum arabic in glycerin-water 1:1. The fluorescent component in the fat and protein soils (see below under *Analytical*) had to be water insoluble but homogeneously dispersible in the soil. The aromatic hydrocarbon perylene met with both requirements. The composition of the standard soils is given below.

Fat soil: 100 g coco fat, Palmin, Margarine-Union GmbH., Hamburg, Germany
100 g condensed milk (10% fat content)

5 g soft drink syrup
2 g stabilizer solution
30 cc perylene in dioxan

Protein soil: 35 g fresh egg albumen
100 g condensed milk (10% fat content)
5 g soft drink syrup
2 g stabilizer solution
30 cc perylene in dioxan

Soot soil: 0.3 g carbon black, Neospectra, K. Herberts, Wuppertal-Barmen, Germany
20 g Esso motoroil HD 30
40 g condensed milk (10% fat content)
2.5 g soft drink syrup.

Washing procedure. The soil was applied with a rubber roller on microscope slides (26 × 76 × 1 mm), which had been cleaned in a mixture of chromic and sulfuric acids. The soiled plates were dried at 100C and checked with the fluorometer. Only those plates, giving a reading between 99–101, were used. The weight of soil was 1.2(6) mg per cm². A circle with a diameter of 2.6 cm was used for the readings.

The plates, by means of a special mount, were attached radially to the vertical shaft of a variable speed laboratory stirrer, their long axis parallel to the shaft. They were immersed into a two liter glass beaker containing 1600 ml detergent solution. The beaker was inside a thermostatic bath for exact temperature control. Since the purpose of the present work was to study the effect of temp and of the type and concentration of detergent, the rate of stirring was kept constant throughout all experiments. In order to make comparisons more meaningful, the velocity at which detergent moved across the glass surface had to be of the same order of magnitude as the rate of flow in commercial bottle washers. Since in most washers, also those of the spray type, the limiting factor is the velocity at which the liquid can flow by gravity out of the neck, the stirring rate was kept quite low so as to ensure laminar flow. It was found that at 62 rpm, the axis of the plate being 3, 1 cm removed from the shaft axis, there was a constant renewal of the liquid in contact with the plate without causing an erosive action. Higher stirring rates caused uncontrollable turbulent flow resulting in irregular cleaning action. After each minute of washing, the glass plates were rinsed with tap water, dried 30 min at 100C, and the fluorescence or light transmittance measured as described below.

Analytical. The incorporation of a fluorescing agent as an indicator in the fat and protein soils made possible accurate measurement by means of a sensitive fluorometer (B. Lange, Berlin) of the quantity of soil on the plate before and after treatment with the detergent. With the soiled plate inserted, the galvanometer reading was set at 100. After every successive treatment with detergent, the plate was placed in the instrument and the galvanometer reading noted. A blank value correction had to be applied to every reading in order to eliminate variations due to slight differences in the quality of the glass plates. It

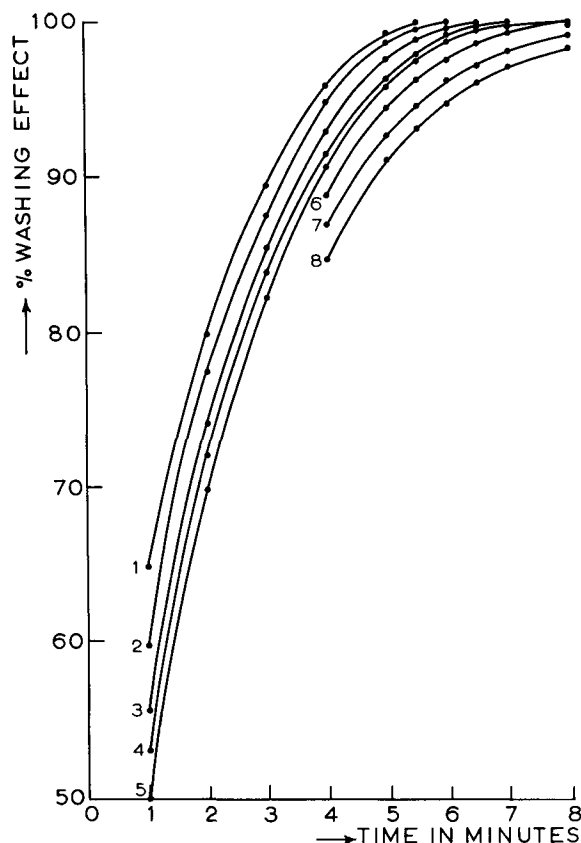


FIG. 1. Influence of temperature and concentration on the effectiveness of NaOH solutions. Fat soil.
 Curve 1, 2, 3: 3% NaOH at 70C, 60C, and 40C.
 Curve 4, 5, 6: 2% NaOH at 70C, 60C, and 40C.
 Curve 7, 8 : 1% NaOH at 60C, and 40C.

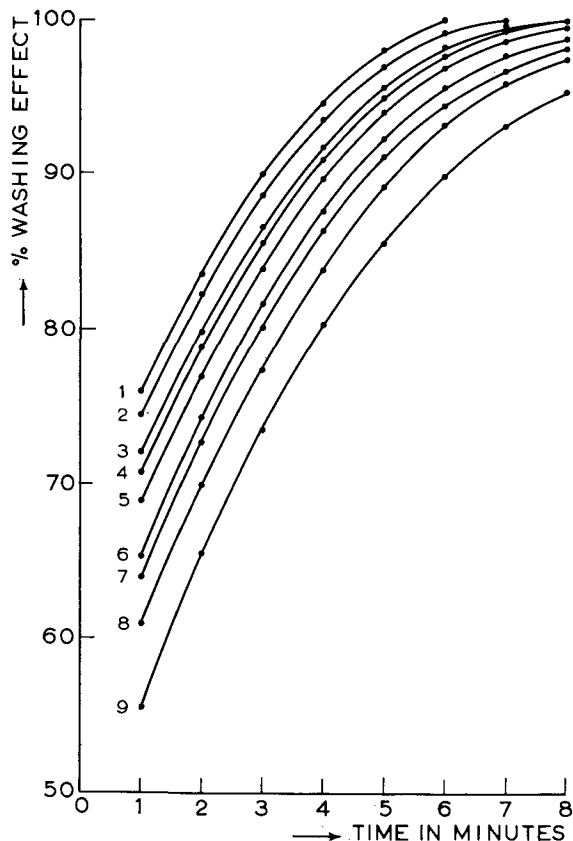


FIG. 2. Influence of temperature and concentration on effectiveness of NaOH solutions. Protein soil.
 Curve 1,2,3: 3% NaOH }
 Curve 4,5,6: 2% NaOH } at 70C, 60C, and 40C.
 Curve 7,8,9: 1% NaOH }

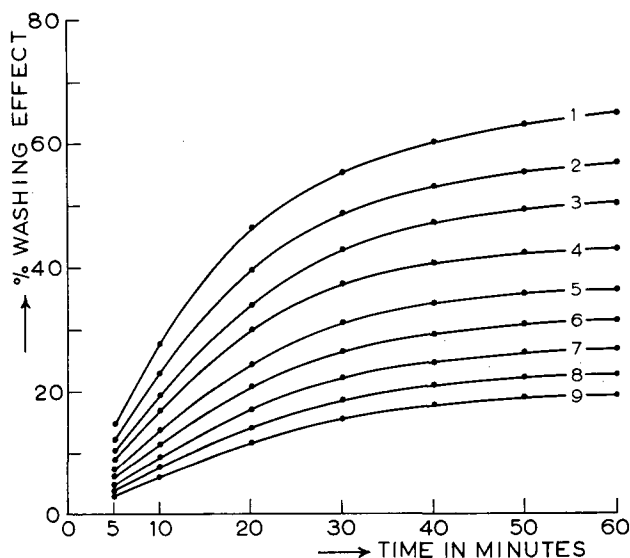


FIG. 3. Influence of temperature and concentration on effectiveness of NaOH solutions. Soot soil.
 Curve 1, 2, 3: temp 70C, NaOH conc 1%, 2%, 3%.
 Curve 4, 5, 6: temp 60C, NaOH conc 1%, 2%, 3%.
 Curve 7, 8, 9: temp 40C, NaOH conc 1%, 2%, 3%.

should be noted that this method would lead to erroneous conclusions if only the surface and not the total fluorescence were measured. The results below prove that this is not the case.

mg soil	Units of intensity	Units of intensity/mg soil
10.5	30.0	2.86
10.2	30.0	2.94
20.2	59.1	2.93
20.4	58.2	2.85
30.3	88.3	2.91
30.1	87.3	2.90

The intensity of fluorescence of six plates on which three different thicknesses of soil were applied (measured by weight of soil as plates were of equal area) is clearly proportional to the quantity of soil on the plate in the range of soil thicknesses used in this work.

The presence of carbon black in the soot soil was shown in a series of preliminary tests to interfere with the accurate measurement of fluorescence. Because of this, the effectiveness of detergents in the soot soil studies was measured by light transmission using a densitometer. The galvanometer was set to read 100 when a carefully cleaned glass plate was inserted in the instrument. Then the transmitted light, through plates soiled with soot soil, was measured before and after successive treatment with detergent. Soiled plates with light transmission (before washing) outside a narrow range set for 100% soiled plates were discarded. Results are expressed in this case in terms of % washing effect as follows: % WE = $100 (a_2 - a_1) / (100 - a_1)$ where a_1 = galvanometer reading before washing and a_2 = galvanometer reading after washing.

Results and Discussion

To establish a base line for comparison purposes, a preliminary series of runs was made, using tap water with total and temporary hardness of 75 and 35 ppm respectively expressed as calcium carbonate. The results showed that at 40C after 4 min not more than 34% washing effect was obtained. After 8 min this had increased to not more than 36.6%.

TABLE III

Effect of Additives on Cleaning Action of NaOH Solutions
in % Washing Effect—Protein Soil
(Conc of combined NaOH and additive 2%; temp 60C)

Mixture	Washing time in min			
	1	2	3	4
80 NaOH + 20 gluconate.....	87.0	95.1	98.6	100
90 NaOH + 10 gluconate.....	86.1	94.6	98.3	100
95 NaOH + 5 gluconate.....	86.0	94.4	98.2	100
98 NaOH + 2 gluconate.....	84.5	93.8	98.0	100
99 NaOH + 1 gluconate.....	84.3	93.6	97.8	100
99.5 NaOH + 0.5 gluconate.....	84.3	93.5	97.6	100
78 NaOH + 2 gluconate + 20 metasilicate.....	89.3	96.8	100	
88 NaOH + 2 gluconate + 10 metasilicate.....	88.4	96.3	100	
79 NaOH + 1 gluconate + 20 metasilicate.....	89.1	96.7	100	
89 NaOH + 1 gluconate + 10 metasilicate.....	88.2	96.1	100	

of polyphosphate. The performance of gluconate containing solutions is further improved by the addition of metasilicate. It is interesting that gluconate is very effective in relatively small proportions (0.5–1% of total detergent), and that increasing its concentration to 20% of total detergent brings about a very small improvement. A mixture of 88% NaOH, 2% gluconate, and 10% metasilicate removed both fat and protein soils completely in 3 min, compared to 7.5 min needed for NaOH alone under otherwise identical conditions. Figure 5 shows that gluconate has a very small effect, and that polyphosphate-metasilicate containing detergents are the most effective for the removal of soot soil.

Cleaning effectiveness of commercial dish washing compounds. It was of interest to apply the present method of detergent evaluation to commercially available dish-washing compounds. Five American and one German product were studied. Results show in Figures 6, 7, and 8. Taking into account the low concentration of 0.2% (as recommended by the manu-

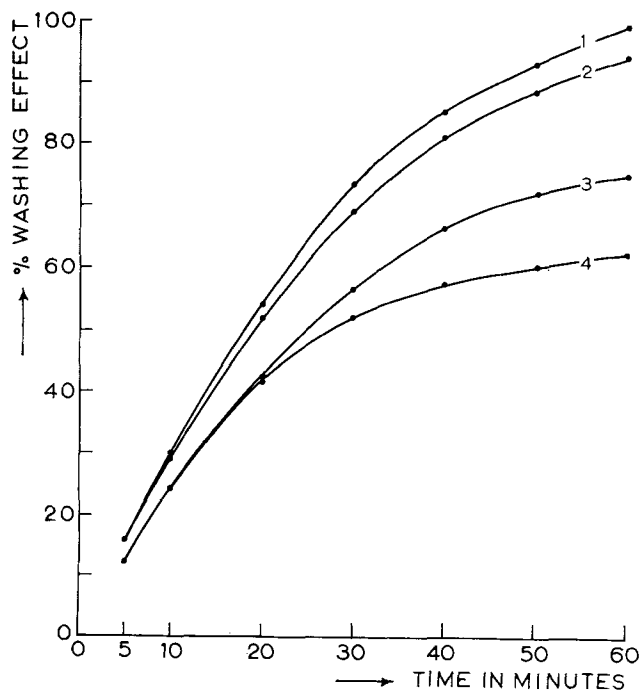


Fig. 5. Effect of additives on cleaning action of NaOH solutions at 70C. Soot soil. Concentration of combined NaOH and additive: 2%.

Curve 1 NaOH:Calgon W:Sodium silicate, 78:2:20. Curve 2 NaOH:Calgon W, 95:5. Curve 3 NaOH:sodium gluconate:sodium silicate, 78:2:20. Curve 4 NaOH:sodium gluconate, 95:5.

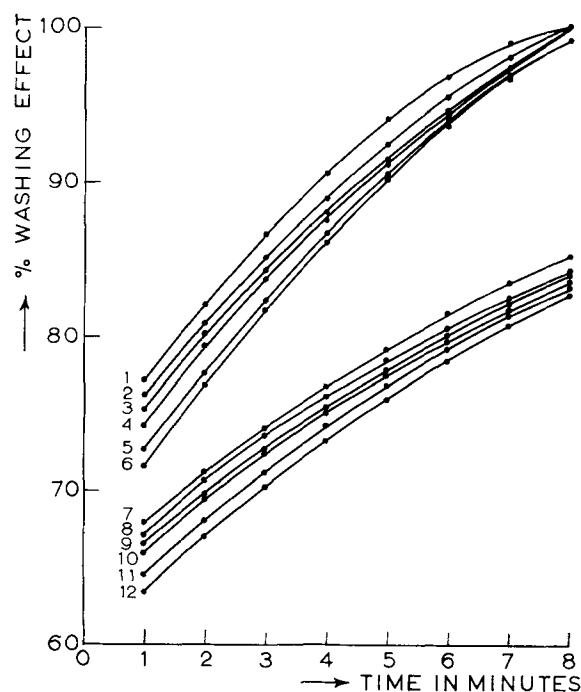


Fig. 6. Cleaning effectiveness of six commercial dish washing compounds in 0.2% solution. Curves 1–6 at 70C. Curves 7–12 at 40C.

facturers for use in household dishwashers), the cleaning effect is rather remarkable. For better comparison with previous results, the tests were repeated at a concentration of 2% with results in Figure 7.

Cleaning effectiveness of NaHCO₃ solutions. NaHCO₃ solutions are traditionally recommended as a mild detergent for inside cleaning of food processing equipment where more aggressive detergents might be unsuitable. A comparison of the results obtained with a 2% NaHCO₃ solution at 20, 40, and 60C with 2% NaOH solution at 60C, is shown in Figure 9 (fat soil) and Figure 10 (protein soil). It is interesting that in both cases NaHCO₃ is more effective during the initial 3.5–4 min of washing, i.e., up to the removal of about 90% of the soil. After this point it seems to be incapable of any appreciable further cleaning.

Stability of detergent solutions. Polyphosphates have a tendency to break down when heated in solution. As bottle washing solutions are generally used over a period of one or more weeks, during which period they are continuously kept at ca. 60C, we used the present method to determine whether any measurable decrease in cleaning efficiency resulted from keeping a 1% solution of a commercial polyphosphate-containing material for 72 hr at 60C. Results below show that a slight decrease in efficiency could be detected.

Solution kept at 60C for:	% Washing effect after 2 min contact-time
hours	
0	90.0
3	89.9
6	89.7
12	89.3
24	88.0
48	87.0
72	86.1

Effect of accumulation of soil in detergent. A practical question is the effect of increasing concen-

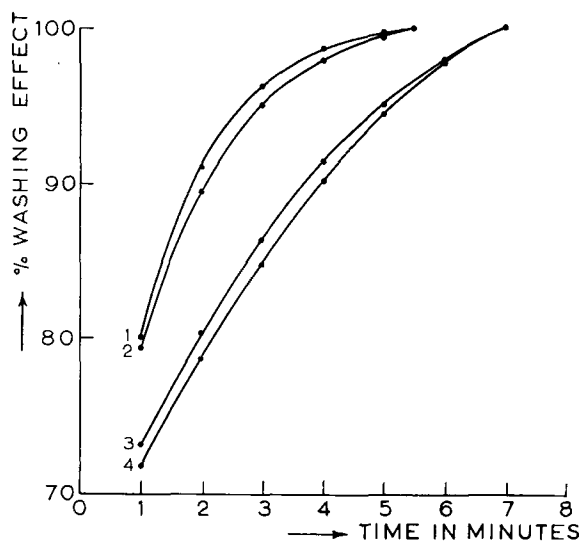


FIG. 7. Cleaning effectiveness of two commercial dish washing compounds in 2% solution. Curves 1 and 2 at 70C. Curves 3 and 4 at 40C.

trations of soil in the detergent on the cleaning efficiency of the latter. For this series of experiments, 7 liters of 1% solution of a commercial compounded detergent were kept at 60C for 10 hr. During this period 10 g of standard fat soil were added to the solution every hour, after which the cleaning efficiency was measured with standard soiled plates with a washing time of 2 min. In this way, the 7 liters of solution contained 100 g of soil after the 10th hour. During the experiment the titratable NaOH content of the solution was kept constant (0.9%) by addition of fresh detergent. Results below show that the cleaning efficiency decreases with increasing amount of soil in the solution, and that titration for NaOH content is not always a dependable measure of the cleaning efficiency of a bottle washer solution.

g fat soil/l solution	after . . . hours at 60C	% Washing effect after 2 min contact-time
0	0	90.0
1.43	1	86.5
2.86	2	84.0
4.28	3	82.0
8.57	6	77.5
11.43	8	75.3
14.30	10	73.0

An attempt to confirm these findings by using detergent solutions removed from a bottle washer operating in a soft drink plant after increasing periods of time was not successful. The cleaning efficiency of the detergent solution after 3 weeks of use was essentially the same as that of the fresh solution. This may be explained by assuming that the concentration of soil in an operating bottle washer remains quite low, even after prolonged periods of operation.

Effect of addition of surface-active compounds. The difficulty in removing soot soil by conventional detergents made desirable an attempt to improve them by the addition of surface-active agents. Weinfurter et al. (1) have reported improved performance by detergents to which Hostapal W (nonyl-phenol-polyglycolether, Farbwerke Hoechst AG.) had been added. Therefore this work was extended to studies at 70C of the NaOH-Hostapal W combinations in Figure 11. Results indicate that even in concentration of

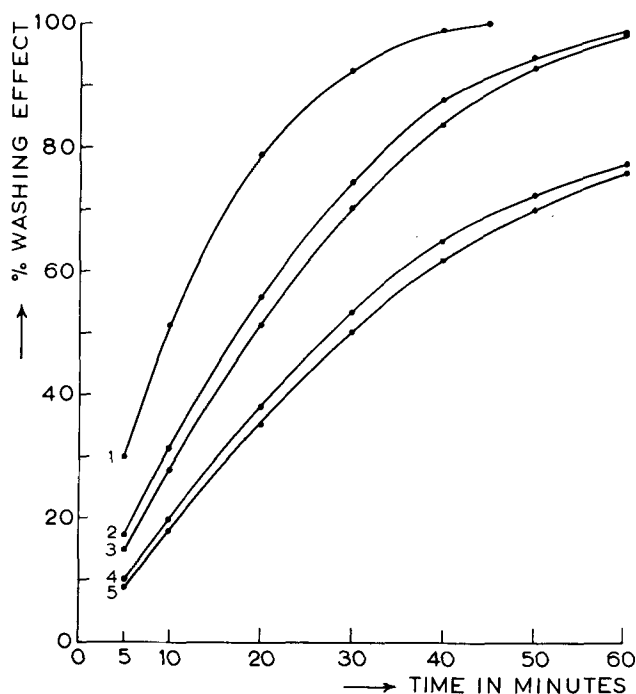


FIG. 8. Cleaning effectiveness of two commercial dish washing compounds at 70C. Curve 2 and 3 in 2% solutions. Curve 4 and 5 in 0.2% solution. Curve 1, 2% of a commercial bottle washing product.

1:30,000, based on dry detergent weight, Hostapal W has a positive effect. The higher concentration (1:3000) shows higher efficiency, but results in a tendency to foam in certain types of bottle washer. The best results were obtained when adding Hostapal W to a commercial detergent in the combinations in Figure 12. The detergent contained 67% NaOH, ca.

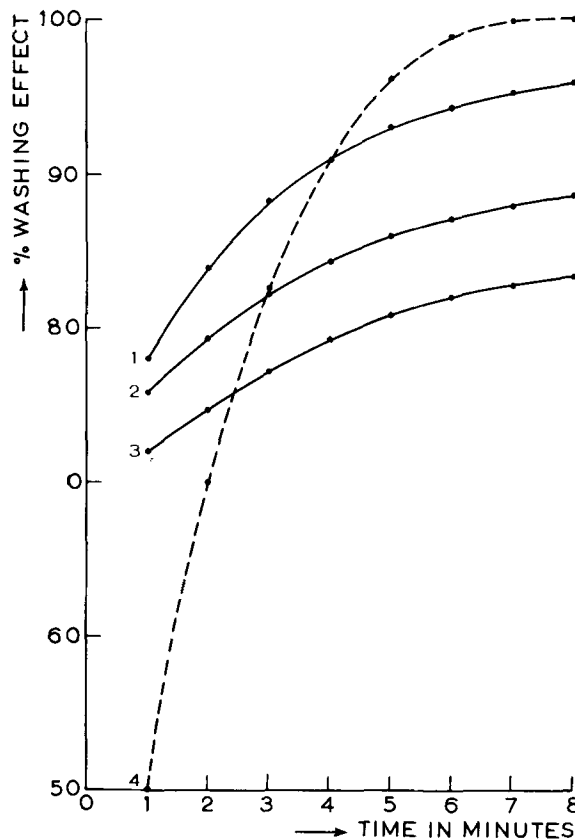


FIG. 9. Cleaning effectiveness of a 2% sodium bicarbonate solution. Fat soil. Curve 1,2 and 3 at 60C, 40C, and 20C. Curve 4, 2% NaOH at 60C.

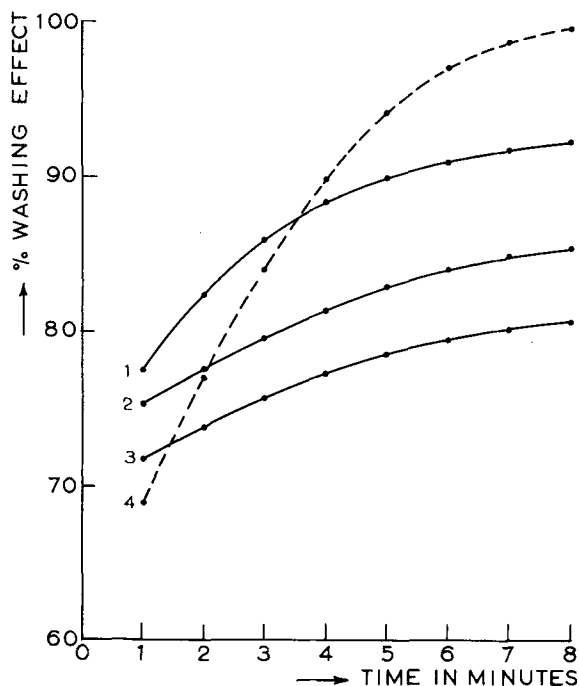


FIG. 10. Cleaning effectiveness of a 2% sodium bicarbonate solution. Protein soil. Curve 1,2 and 3 at 60C, 40C and 20C. Curve 4, 2% NaOH at 60C.

10% polyphosphates, silicates, and sodium carbonate.

Effect of application of ultrasonics. A different approach to the problem of removal of soot soil was the use of ultrasonics in conjunction with various detergent solutions. The equipment (Lehfeldt & Co. G.m.b.H., Heppenheim, Germany) consisted of a 12-liter container with a built-in barium titanate sonic generator, connected to a 40 KC high frequency generator. The detergent solution was contained in a 2-liter glass beaker, in which the soiled test plates rotated at 62 rpm, as in all previous experiments. The medium between the beaker and the container was thermostated deaerated water. Table IV summarizes results obtained with various detergents at 40C and 60C. The drastic increase in cleaning efficiency by the use of ultrasonics is obvious and needs no further comment.

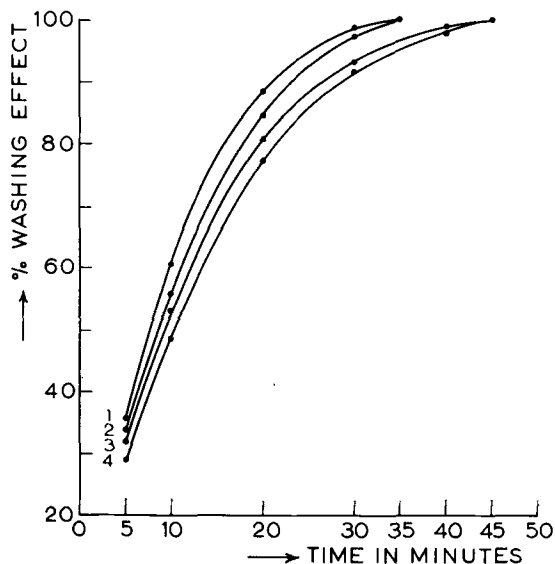


FIG. 11. Effect of addition of a surface active compound on the cleaning effectiveness of NaOH solutions at 70C. Curve 1 and 2, 3% and 2% solution of NaOH + Hostapal W (1:3000 by weight of dry NaOH). Curve 3 and 4, 3% and 2% solution of NaOH + Hostapal W (1:30,000).

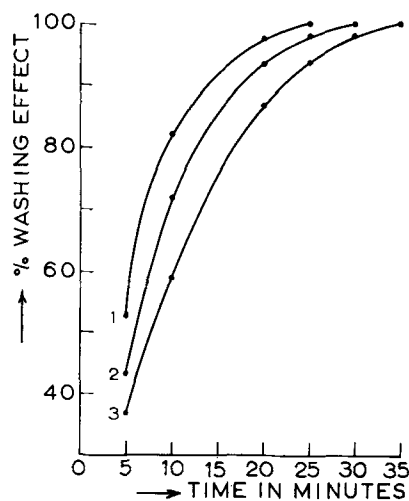


FIG. 12. Effect of addition of Hostapal W to cleaning effectiveness of a commercial detergent consisting of NaOH and a bottle washing product (67:33). Curve 1 and 2, Hostapal W added 1:3000, and 1:30,000. Curve 3, no additive.

Conclusions

Satisfactory techniques were developed for quantitatively measuring the rate at which various detergent solutions would remove synthetic soils from a glass surface.

Fat and protein soils were removed from glass in approximately equal times, but removal of a soot soil made up to imitate the soil of smoky industrial areas, where bottles had proved difficult to clean, took nearly 10 times as long as did removal of the other soils.

Commercial detergents and detergents made up of NaOH with additives such as metasilicate, gluconate, and polyphosphate removed soils up to twice as fast as did NaOH alone.

The temperature gradient for the action of alkaline detergents was low. Increasing the temperature from 40–70C reduced the time required to clean the glass by about one-third.

In the concentration range of 1–3% speed of cleansing increased as the detergent concentration increased, but not in direct proportion. For practical purposes a detergent concentration of 2% would seem adequate for industrial usage.

An alkali as mild as sodium bicarbonate showed a slight but definite detergent action.

Commercial dishwashing compounds used in the recommended concentration of 0.2% exhibited a cleansing power of the same order of magnitude as that of a 2% alkaline detergent; however, large increases in concentration of the dishwashing compound

TABLE IV
Effect of Ultrasonics on Cleaning Efficiency of Detergent Solutions in % Washing Effect—Soot Soil

Temp °C	Mixture	Contact-time in seconds			
		30	60	90	120
40	2% NaOH.....	84.1	93.1	97.5	100
40	2% (98 NaOH + 2 gluconate).....	91.1	97.4	100	
40	2% commercial detergent.....	88.7	96.4	100	
40	2% commercial detergent.....	92.7	98.0	100	
40	2% commercial detergent plus Hostapal W (1:30,000).....	95.9	100		
60	2% NaOH.....	86.2	95.4	100	
60	2% (98 NaOH + 2 gluconate).....	93.1	100		
60	2% commercial detergent.....	91.2	100		
60	2% commercial detergent.....	94.6	100		
60	2% commercial detergent plus Hostapal W (1:30,000).....	100			

did not strikingly decrease the time required for cleaning. The action of commercial dishwashing compounds seemed to have a greater temperature gradient than that of an alkaline dishwashing compound.

The addition to a detergent bath of nonyl-phenol-polyglycol ether (Hostopal W) in extremely low concentrations caused a definite increase in the rate of detergent action.

The application of ultrasonic energy to a given

detergent bath increased the rate of detergent action as much as 30-fold.

ACKNOWLEDGMENT

Continued guidance during the course of this study from C. A. Shillinglaw.

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[Received May 7, 1962—Accepted September 16, 1963]

Search for New Industrial Oils. VIII. The Genus *Limnanthes*

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Abstract

Seed oils from most of the known species and varieties of *Limnanthes* were analyzed for their fatty acid content. Each contained at least 95% acids with more than 18 carbon atoms. The major component acid, *cis*-5-eicosenoic, ranged 52-77% of the acids present. Seeds of all species examined contained thioglucosidic precursors of volatile isothiocyanates, liberated by the action of mustard seed enzymes on the meal. One species also yielded a small amount of an oxazolidinethione-like compound of the type associated with enzyme-treated rapeseed meal.

Introduction

OIL FROM SEED of *Limnanthes douglasii* R.Br. was reported as unusual because 94% of its acids exhibited longer retention times than linolenic acid, the slowest C₁₈ component of common oils, in GLC on a polar substrate (4). More detailed investigation led to characterization of the major components as three new acids: *cis*-5-eicosenoic; *cis*-5-docosenoic; and *cis*-5, *cis*-13-docosadienoic (1,14) in addition to the known *cis*-13-docosenoic (erucic) acid. The unusual position of unsaturation in these long-chain acids and the very small quantity of acids containing less than 20 carbon atoms suggest that the oil may be a useful new raw material for processing into industrial products. Exploratory studies on wax esters prepared from *L. douglasii* seed oil indicate their striking similarity to the liquid wax of jojoba seeds (12).

Profitable use of the oil-free meal could have significant bearing on the industrial acceptance of a new oilseed. The value returned by the meal could be reflected in lower prices for the oil, thus improving the competitive position of the oil and making it economically acceptable for a broader variety of applications. Since meal from *L. douglasii* contains lysine and methionine in amounts comparable to the legumes (15), it should have value as a component of feed mixes. However, *m*-methoxybenzyl isothiocyanate, produced by enzymatic hydrolysis of a thioglucoside in *L. douglasii* seed (5), if not removed, may be detrimental to the quality of the seed meal in the same manner that similar compounds affect the use of mustard meals (2). Such removal might effectively be carried out by a process recently developed at the

Northern Laboratory that eliminates volatile allyl isothiocyanate from mustard meal (13).

The potential value of *Limnanthes* as an oilseed prompted a study of variation in oil, protein, and thioglucoside contents and in composition of the oil in seed from all available species.

Botanical Nature of the Genus

The genus *Limnanthes* as classified by Mason (9) includes eight species of annual herbs native to the Pacific Coast. All species germinate in the fall or winter and require relatively cool weather during the growing season. Hot weather in late spring adversely affects them. An ecological survey of the wild populations disclosed a wide range among varieties in adaptability to different soil and moisture conditions. Such diversity indicates promise for successful introduction to cultivation. Also there is sufficient variability in growth form and seeding characteristics to indicate success for the selection of superior strains for commercial production. Genetic crosses between several varieties have already been demonstrated (9). This compatibility is important in developing cultivated varieties; nearly all cultivated crops result from crossing varieties and species either intentionally or inadvertently. *L. douglasii*, a garden ornamental, is the only cultivated species. Figure 1 shows a closeup of a cultivated plant and a dense wild stand of *L. douglasii* var. *nivea*. The botanical aspects of this genus as a potential source of new oilseed crop will be published elsewhere (6).

Materials and Methods

Seeds used in the present survey, except for a few samples of *L. douglasii* bought from a commercial supplier, were obtained by collection from wild plants in the spring of 1962.

Seeds were cleaned and analyzed as previously reported (4). Methanolysis of the oil with HCl as catalyst yielded methyl esters of the fatty acids, which were analyzed by GLC (10). Results are reported as percentage of the area under the curve attributable to a given methyl ester.

Enzyme treatment of the seed meals and estimation of the liberated volatile isothiocyanates and oxazolidinethiones were performed essentially as described by Wetter (16,17). A slight modification (3) allowed investigation by paper chromatography of a portion of the thiourea derivatives of the steam-distilled isothiocyanates (8).

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