

BULLETIN No. 257.

DECEMBER, 1904.

New York Agricultural Experiment Station.

GENEVA, N. Y.

THE COMPOSITION OF COMMERCIAL SOAPS IN
RELATION TO SPRAYING.

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SUMMARY.

1. **Object.** The object of the work discussed in this bulletin was to ascertain why commercial whale-oil soaps in some cases fail to destroy insects and in some cases cause injury of foliage.

2. **What a Soap is.** A soap is made by treating a fat or oil with an alkali, as caustic soda or potash. A soap is a chemical compound formed by the union of an alkali and the fatty acid or acids contained in a fat or oil.

3. **Results of Analysis of Commercial Whale-Oil Soap.** The important constituents of a soap in relation to spraying are (a) water, (b) actual soap, and (c) free alkali. In the case of nine samples of commercial whale-oil soap, the percentage of water varied from about 11 to 55 per ct.; of actual soap from about 15 to 60 per ct.; of free alkali from nothing to 1.30 per ct. Two different lots of soap from the same factory contained 36.79 and 53.13 per ct. of water and 24.06 and 46.28 per ct. of actual soap.

4. **Result of Variation in Composition of Commercial Whale-Oil soaps.** In making solutions of different commercial whale-oil soaps, one can not be sure of having a uniform strength of solution and this lack of uniformity seriously affects their value for spraying purposes.

5. **Home-manufacture of Fish-Oil Soap.** In order to have a soap of uniform composition, the following

formula may be suggested: Caustic soda, 6 pounds; fish oil, 22 pounds; water, $1\frac{1}{2}$ gallons. This will make 40 pounds of soap. Certain precautions given in detail in the text of the bulletin should be carefully observed.

6. Experiments in using Home-made Soap in Spraying. The home-made soap, when used at the rate of one pound in seven gallons of water, gave entire satisfaction in every way on the foliage of apple, pear, plum, currant, cherry and peach trees. The foliage was not injured and plant lice were destroyed.

7. Experiments in Spraying with Soap containing Free Alkali. Soaps were made so as to contain 1, 2, 5, 10, 20 and 50 per ct. of free alkali. These were used in the same strength of solution and on the same kinds of foliage as given above. Injury was done when the free alkali reached 10 per ct. Little injury was done by the use of soap containing 5 per ct. or less of free alkali.

8. Cost of Home-made Soap. Caustic soda can be purchased at $4\frac{1}{2}$ cents a pound and fish-oil at 26 to 30 cents a gallon. On the basis of these figures, the cost of the materials used in making one pound of fish-oil soap is about $2\frac{3}{4}$ cents.

9. Advantages of Home-made Fish-Oil Soap are (1) greater uniformity of composition, (2) greater reliability, (3) decreased cost.

INTRODUCTION.

The work embodied in this bulletin was suggested by the complaints that have been made in respect to the unsatisfactory results frequently experienced in the use of so-called whale-oil soap when used on orchards for the purpose of destroying certain forms of insects. The disappointing results reported vary in character; in some cases the insects are only incompletely destroyed; in other cases, the foliage is killed and the trees also. The uncertainty of the results of applying this remedy has caused no little uneasiness among fruit growers and numerous letters have come to this Station asking for information in regard to the use of whale-oil soap. As a result of this condition, the Station entomologist, Mr. P. J. Parrott, suggested that we take up the subject for investigation.

There are on the market many different brands of whale-oil soap, and it occurred to us that there must be marked variations in the character of different brands to account for the great difference reported in the results of their use. There is no known recognized standard of composition for this class of soaps and, as a starting point of our investigation, it seemed necessary to obtain a more complete knowledge of the composition of the varieties of whale-oil soap found in the market.

It may be stated here at the outset that many commercial whale-oil soaps contain no whale-oil proper, but the term "whale-oil" is applied to any kind of fish-oil soap, and the oil of such fish as the menhaden has come to be largely used as a substitute for more expensive oils.

Before taking up our chemical study of soaps, we will call attention, in passing, to the reason why fish-oil soaps are used as extensively as they are. Destructive insects cause injury in two ways, first by destroying portions of the foliage by direct biting or cutting out pieces of the leaves, and, second, by sucking the juices of the plant. The insects causing injury in the first way are readily killed by applying insect poisons to the foliage. The sucking insects, among which the San José scale

and plant lice are the most common, are not killed by the application of ordinary insect poisons. They can be killed only by what is known as a "contact remedy," which is either a fluid that penetrates the spiracles or breathing holes, filling them up and thus causing death, or is a water-solution of some substance, which, when the water evaporates, remains as a thin coating over the insects, thus covering the spiracles and preventing breathing. Whale-oil soap is a contact remedy of the second kind and, owing to the rapid spread in recent years of plant lice and scale, has become most important on account of its very extended application, being used probably more than any other contact remedy.

It is supposed by some that whale-oil soaps possess in themselves some peculiar value for destroying insects, and this opinion might appear to be justified by the extreme offensiveness of the odor, but as a matter of fact any good soap possesses just as much value for this purpose, the preference shown for fish-oil soaps being due solely to their relative cheapness.

THE COMPOSITION OF WHALE-OIL SOAPS.

There were collected for analysis nine different brands of commercial whale-oil soap, some being obtained directly from manufacturers, some by private purchases and others from supplies on hand at the Station.

WHAT SOAPS IN GENERAL ARE.

Before presenting the results of analysis, we will consider briefly the chemistry of soaps. Soaps are made by treating fats or oils with a caustic alkali, caustic soda being used in making hard soap and caustic potash in making soft soap. A real chemical combination occurs between the alkali and the fat or oil. Thus, a fat or oil is generally a mixture of several compounds, each of which contains glycerine in chemical combination with certain acids, most commonly what are known as "fatty" acids. When a fat or oil is treated with caustic soda, the sodium takes the place of the glycerine and unites with the fatty acids, forming a sodium compound of each of the fatty acids, and the glycerine that was in combination is set free as

glycerine. In some cases, boiling is necessary to cause the alkali and fatty acid to combine ; in other cases, the action takes place at ordinary temperatures. A soap is, therefore, a chemical compound formed by the union of an alkali with the fatty acid or acids of a fat or oil. Other substances are frequently added to soaps for various purposes, such as resin, water, coloring matter, perfume, etc.

EXPLANATION OF TERMS USED IN ANALYSIS OF SOAPS.

The terms commonly used in expressing the results of analysis of a soap, when it is desired to determine its fitness for spraying purposes are the following: (1) Water, (2) fatty acids expressed as anhydrides, (3) sodium oxide combined as soap, (4) potassium oxide combined as soap, (5) resin, (6) free acid estimated as oleic acid, (7) free alkali.

(1) *Water in soap.*—It is desirable to know the amount of moisture in soap in order to know its value for spraying purposes, since the greater the amount of water in the soap, the more soap will be needed to make a soap solution of a certain strength.

(2) *Fatty acids expressed as anhydrides.*—Under this heading, we indicate simply the proportion of fatty acids present in the soap.

(3) *Sodium oxide combined as soap.*—In order to know the kind and amount of alkali present in a soap, it is necessary to determine the amount of sodium, expressed as oxide, that is actually present in combination in the soap.

(4) *Potassium oxide combined as soap.*—When a soap is guaranteed to contain potash, it is important to ascertain how much is present, since potash costs more than caustic soda. In an ordinary soda soap, it is not important to determine the potash.

(5) *Resin.*—To many soaps resin is added apparently for the purpose of enabling the soap to hold water, making it harder and of increasing the weight.

(6) *Free fatty acid.*—In making a soap, more fat or oil may be used than can combine with the alkali used and then some uncombined fat or oil will be left over. This is indicated under the expression "free fatty acid." The same condition may occur when the combination of fat and alkali is incomplete.

(7) *Free alkali.*—When more alkali is used than can combine with the fat or oil used or when the combination is incomplete, free alkali is left in the soap. This condition in spraying soaps may prove injurious to foliage.

RESULTS OF ANALYSIS OF WHALE-OIL SOAPS.

In the following table, we present the results of analysis of 9 samples of commercial whale-oil soap. Ordinary impurities were not determined. Potash was estimated only in those advertised as potash soaps. The amount of actual soap is found by adding the constituents, anhydrides of fatty acids, soda and potash.

TABLE I.—GIVING RESULTS OF ANALYSIS OF WHALE-OIL SOAPS.

No. of sample.	Water.	Actual soap.	Fatty acids expressed as anhydrides.	Soda (Na ₂ O) combined as soap.	Potash (K ₂ O) combined as soap.	Free fatty acids.	Free alkali as soda (Na ₂ O).	Resin.
	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>
1	11.15	59.27	50.84	8.43	0	11.14	0.00	12.65
2	20.38	36.66	25.87	10.79	0	3.95	0.00	15.60
3	28.39	14.90	8.05	6.85	0	0.00	1.30	20.58
4	29.43	50.27	39.11	11.16	0	14.66	0.00	4.99
5	29.75	19.66	12.07	7.59	0	10.01	0.00	33.17
6	36.79	46.28	35.82	4.88	5.58	12.41	0.00	8.25
7	52.74	25.80	16.40	2.33	7.07	10.72	0.00	10.57
8	53.13	24.06	19.12	1.95	2.99	17.20	0.00	—
9	54.85	24.11	15.27	1.89	6.95	9.02	0.00	7.98

The tabulated data of special interest that enable us best to estimate the value of a soap for spraying purposes are the following: Water, actual soap, free fatty acids and free alkali. What does this table reveal in regard to the presence of these various constituents in the different soaps?

(1) *Water* in the nine samples varies from 11.15 to 54.85 per ct. No. 6 and No. 8 are different lots of the same brand of soap, but the content of water differs over 16 per ct.

(2) *Real soap* in the different samples varies from 14.90 to 59.27 per ct., a range of difference even greater than in the case of the water in these soaps. In samples 6 and 8, which represent different lots of the same manufacturer's material, the real soap is nearly twice in amount in No. 6 what it is in No. 8.

(3) *Free fatty acids* varied from nothing to 17.20 per ct., in-

dicating in most cases that the oil was used in amount more than sufficient to combine with alkali.

(4) *Free alkali* was generally absent, being found in only one soap and then not in excessive amount, indicating that not enough oil was employed to combine fully with the alkali.

It is evident, then, that these whale-oil soaps, which were actually found offered for general sale in the market, are absolutely unreliable for anything like uniform composition. An inspection of the data in the preceding table must readily reveal why a fruit-grower who uses a soap like No. 3, containing less than 15 per ct. of soap, will fail to get satisfactory results as compared with the one who uses No. 1 or No. 4, which contain over 50 per ct. of actual soap. A man purchasing No. 6, containing over 46 per ct. of actual soap, and using it with success might at the next purchase get No. 8, the same brand as No. 6, but containing only 24 per ct. of soap, and then be puzzled to know why the soap failed to destroy the insects. Some of these soaps when used according to the usual directions, give a solution four times as strong as some of the other soaps. Suppose, for illustration, one uses No. 1 soap at the rate of one pound to seven gallons of water; in order to have a solution contain the same amount of soap, it would be necessary to use four pounds of No. 3 for seven gallons of water. In the case of No. 6 and No. 8, the same directions for use accompanied both lots and yet one contained twice as much actual soap as the other.

The variation of the soaps in water content did not account for all the differences of actual soap. Thus, No. 3, No. 4 and No. 5 contain about the same amount of water but the actual soap in them varies from 14.90 to 50.27 per ct.

It is a fact that very few makers of commercial whale-oil soaps are willing to guarantee the composition of their product. It would, therefore, appear that horticulturists cannot depend upon the whale-oil soaps in the market as possessing a standard, or uniform, composition. The question arises as to how one can know how much commercial whale-oil soap to use under the circumstances. The only practicable suggestions are either to make up solutions of different strength and try them in a small way on foliage, thus ascertaining how much soap to use, or else to purchase reliable materials and make soap for ones own use.

EXPERIMENTS IN THE HOME-MANUFACTURE OF FISH-OIL SOAP.

It was thought desirable under the circumstances to try some experiments in making fish-oil soap and to find a formula that could be recommended as giving results in every way satisfactory. Two formulas were tried. The materials used were common fish-oil, caustic soda and water. The quantities given are based on a finished product of 40 pounds of soap. In making the soap, the caustic soda is completely dissolved in the given amount of water and the fish-oil is then added gradually under constant and vigorous stirring. The combination occurs readily at ordinary summer temperatures and the operation is soon completed. The mixing may be done in any receptacle sufficiently large to contain the whole amount of material. It would probably not be desirable to attempt to make more than 20 to 40 pounds at a time, since the difficulty of thoroughly stirring a larger mass would tend to make a complete combination less sure, thus rendering liable the presence of too much free alkali. *Complete and thorough stirring is essential to success.* Caustic soda should be handled with precaution, since in concentrated form it easily injures the skin.

NO. 1. FORMULA FOR MAKING 40 POUNDS OF FISH-OIL SOAP.

Caustic soda.....	6 pounds.
Water.....	1½ gallons.
Fish-oil.....	22 pounds.

This was found to show on analysis,—

Water.....	24.91 per ct.
Actual soap.....	61.57 “ “
Free alkali.....	0.74 “ “

A 20-pound lot made up at another time contained 0.62 per ct. of free alkali.

No. 2. Another mixture was made containing twice as much caustic soda and less fish-oil. This contained,—

Water.....	23.36 per ct.
Actual soap.....	47.79 “ “
Free alkali.....	11.22 “ “

EXPERIMENTS IN USING HOME-MADE SOAPS IN SPRAYING.

Experiment 1.—Action on aphids of willow.—Soap No. 1 was used in solutions of three different strengths (one pound of soap in two, five, and seven gallons of water) upon willow leaves

infected with the willow aphid (*Lachnus salicicola* Uhler). The insects were completely destroyed by each of the three solutions. The success of this home-made soap in solution of at least one pound of soap in seven gallons of water was thus shown in destroying aphid.

Another point, however, demanded attention, the effect of free alkali in a soap solution upon the foliage itself. To test this a series of additional experiments was carried on.

Experiments testing action of home-made soap containing different amounts of free alkali upon foliage.—In the following set of experiments, the solutions used contained one pound of soap in seven gallons of water. Soap No. 2, containing 11.22 per ct. of free alkali, was used without any addition of alkali. Soap No. 1 was used in its normal condition, containing 0.75 per ct. of free alkali, and also with added quantities of caustic soda, making the amount of free alkali in the soap 1, 2, 5, 10, 20 and 50 per ct. of the soap.

(1) June 22, apple, pear, plum and currant leaves were sprayed with solutions of soap containing 0.75, 1, 2, 5 and 10 per ct. of free alkali. A fine rain was falling while the trees were being sprayed and the results of the experiment must be interpreted with reference to this condition. The leaves were examined on the second and third day after spraying. On the second day after spraying, only the young apple leaves showed signs of burning and that was by the one solution made from soap containing 10 per ct. of free alkali. When examined on the third day after spraying, the apple leaves appeared the same as on the previous day, the plum and currant leaves showed no appreciable harm, and the pear foliage was unharmed except for a slight burning at the ends of the leaves by the solution of the soap containing 10 per ct. of free alkali.

(2) June 23, apple, pear, plum and cherry foliage was dipped in solutions of soap containing 0.75, 2, 5, 10 and 20 per ct. of free alkali and also in a solution of soap No. 2 containing 11.22 per ct. of free alkali. When examined on the next day, no harm was shown by any of the leaves except the young leaves of the apple in the case of the largest amounts of free alkali. It was noticed that a lady-bird beetle on the foliage was killed by

the solution of the soap that contained 20 per ct. of free alkali. When examined on the second day after spraying, the following results were observed :—The apple leaves treated with soap containing 0.75, 2 and 5 per ct. of free alkali were not injured ; those treated with the soap containing 10 and 11.22 per ct. of free alkali were slightly burned, while the soap containing 20 per ct. of free alkali caused serious injury.

The pear foliage suffered no injury from soap containing five per ct. or less of free alkali, while injury was caused by the soap containing 10 per ct. or more of free alkali, the extent of injury increasing with the amount of free alkali present.

The plum foliage suffered no injury except very slight burning in the case of the solution made from the soap containing 20 per ct. of free alkali.

The cherry leaves were injured by solutions made from soap containing 10 per ct. or more of free alkali.

(3) June 24, apple, pear, plum, currant, cherry, and peach leaves were treated with a solution made from a soap containing 50 per ct. of free alkali. In every case, the leaves were badly burned, as might be anticipated.

These results are presented below in tabulated form.

TABLE II.—SHOWING RESULTS OF ACTION OF FREE ALKALI IN SOAP ON FOLIAGE.

Kind of foliage.	When treated.	When examined.	Extent of injury done to foliage by free alkali in soap.							
			Per ct. of free alkali in soap from which solutions were made.							
			0.75	1	2	5	10	11.22	20	50
Apple	June 22	June 24	None	None	None	None	Some	—	—	—
"	"	" 25	"	"	"	"	"	—	—	—
Pear	"	" 24	"	"	"	"	None	—	—	—
"	"	" 25	"	"	"	"	Slight	—	—	—
Plum	"	" 24	"	"	"	"	None	—	—	—
"	"	" 25	"	"	"	"	"	—	—	—
Currant	"	" 24	"	"	"	"	"	—	—	—
"	"	" 25	"	"	"	"	"	—	—	—
Apple	June 23	" 24	"	—	"	"	Some	Some	Some	—
"	"	" 25	"	—	"	"	"	"	Serious	—
Pear	"	" 24	"	—	"	"	None	None	Slight	—
"	"	" 25	"	—	"	"	Slight	Some	Serious	—
Plum	"	" 24	"	—	"	"	None	None	None	—
"	"	" 25	"	—	"	"	"	"	Slight	—
Cherry	"	" 24	"	—	"	"	None	None	None	—
"	"	" 25	"	—	"	"	Some	Some	Serious	—
Apple	June 24	" 27	—	—	—	—	—	—	—	} Very serious
Pear	"	" "	—	—	—	—	—	—	—	
Plum	"	" "	—	—	—	—	—	—	—	
Currant	"	" "	—	—	—	—	—	—	—	
Cherry	"	" "	—	—	—	—	—	—	—	
Peach	"	" "	—	—	—	—	—	—	—	

The results of the experiments described above indicate that the presence of free alkali to the extent of five per ct. in soap does not injure foliage when the soap is made into a solution of one pound of soap in seven gallons of water. Comparatively little harm is done even when the amount of free alkali in a soap amounts to 10 per ct., the soap solution being of the same degree of dilution. It can readily be seen, therefore, that home-made soap No. 1, containing less than one per ct. of free alkali, can be safely used on all the varieties of foliage experimented with and can also be relied upon to destroy plant lice, when used in the form of a solution of one pound of soap to seven gallons of water.

COST OF MATERIALS USED IN HOME-MADE SOAP.

Caustic soda of good commercial quality (74 per ct.) can be purchased from the Penn Chemical Co., 1322 Washington Ave., Philadelphia, Pa., at about four cents a pound, f. o. b., put up in

50-pound cans. Making liberal allowances for freight and any incidental expenses, the cost of caustic soda should not exceed $4\frac{1}{2}$ cents a pound. It can be purchased at drug stores for about 6 cents a pound.

We have been at considerable trouble to learn where fish-oil can be purchased. It can be furnished in barrel lots by the following parties:

Nehemiah B. Cook, 148 Front St., N. Y. City.

Swan & Finch Co., 151 Maiden Lane, N. Y. City.

Refined fish-oil can be purchased in barrel quantities at 29 cents a gallon f. o. b. Crude fish-oil can be purchased under the same conditions at 25 cents a gallon and answers the purpose very satisfactorily.

From these data, we can estimate the cost of materials used in making soap according to the formula given, making some allowance for cost of shipping materials.

6 pounds caustic soda at $4\frac{1}{2}$ cents a pound.....	\$0.27
22 pounds (about 3 gallons) fish-oil at 29 cents a gallon..	0.87
Total cost of materials used in making 40 pounds of soap..	\$1.14
Cost of one pound of soap.....	2.85 cents.

Commercial whale-oil soap costs at retail in small quantities 10 cents a pound; in larger quantities, six cents a pound. In barrel-lots, amounting to 350 to 400 pounds, whale-oil soap can be purchased in New York City at $4\frac{1}{2}$ cents a pound, and fish-oil soap at $3\frac{1}{2}$ cents a pound.

It would, therefore, appear that some saving may be effected in the home-manufacture of fish-oil soap for spraying purposes. Even if no saving could be made by home-manufacture, an article of greater uniformity and reliability could be secured and this would generally result in marked economy in comparison with using commercial soaps of uncertain and very variable composition.