Saponification Value Determination of Difficultly Saponifiable Drying Oil Products

JOHN N. SHAW and MARVIN W. FORMO, Archer-Daniels-Midland Company,
Minneapolis, Minnesota

WITH the increased use of more complex drying oil products, such as dicyclopentadiene copolymers and alkyds, styrene copolymers and alkyds, maleic modified drying oils, etc., the need for a straight-forward method for their quantitative saponification becomes apparent.

There have been several recent papers giving so-called "drastic" saponification to difficultly saponifiable esters. Shaefer and Balling (1) used an approximately 0.8N solution of potassium hydroxide in a blend of 92% of diethylene glycol and 8% of phenetole by volume to obtain concordant results on several samples of rosin esters, such as rosin methyl esters. Shaefer and Piccard (2) studied the saponification of dibornyl phthalate and difficultly saponifiable esters of abietic acid other than ester gum (the glycerol ester of rosin). They employed reagents formed by dissolving sodium in tert-butyl alcohol and by dissolving sodium methoxide in a solution of methanol and cyclohexanol to obtain theoretical saponification values of these products.

The use of n-butyl alcohol as a supporting solvent for saponification was first suggested by Pardee and Reid (3). A series of simple esters, such as ethyl benzoate and benzyl formate were saponified in methyl, ethyl, propyl, isobutyl, and n-butyl alcohol solutions of the corresponding alkoxides. Their work indicated that use of n-butyl alcohol as the saponification solvent gave the most consistent and reliable results.

During ester saponification, using an alcoholic alkali, the first reaction is alcoholysis to give the corresponding ester of the solvent alcohol. The subsequent saponification step is much slower.

In the absence of catalysts the alcoholysis reaction is extremely slow. It was demonstrated by Henriques (4), Bertoni (5), Reid (6), Anderson and Pierce (7), and many others that strong acids and sodium alkoxides greatly increase the rate of the alcoholysis reaction. Reid (6) concluded that alcoholysis, using sodium alkoxides as catalysts, takes place approximately 4,000 times as rapidly as alcoholysis using equivalent amounts of hydrochloric acid.

Anderson and Pierce studied the ethanolysis of methyl benzoate, using a solution of sodium ethoxide in ethyl alcohol. They concluded that alcoholysis is about 1,500 times as rapid as saponification.

Pardee and Reid (3) pointed out that use of methyl and ethyl alcohols as solvents for saponification would tend in many cases to give low saponification values because of the volatility of the methyl and ethyl esters, which are formed almost instantaneously. Use of n-butyl alcohol minimizes loss of saponifiable material by decreasing the volatility of the esters formed during the alcoholysis step.

A study of the saponification of various oils, such as linseed, soybean, palm, and coconut, was carried out by Pardee, Hasche, and Reid (8). Slightly higher but quite concordant saponification values were obtained, using n-butyl alcohol as the solvent rather than the standard ethyl alcohol. All results were obtained at steam bath temperature.

Ethyl alcohol, as a medium for saponification, obviously is excellent when used for the normal unprocessed drying oils and even for some of the simple, chemically modified drying oil products. It is important that adequate condenser systems be employed during saponification to minimize the loss of the volatile alkyl esters formed by alcoholysis.

Several shortcomings are involved in the use of ethyl alcohol. It is not a good fat solvent and most samples are not soluble in all proportions in the ethyl alcohol-potassium hydroxide reagent at saponification temperatures. In systems containing dibasic acids the potassium half salt may precipitate during saponification, resulting in incomplete reaction. Many drying oil products form hard, resinous, insoluble masses in the bottom of the reaction flask during the saponification, tending to occlude saponifiable material and resulting in low observed saponification values. During titration, using aqueous systems, insoluble material may be deposited on the bottom and sides of the titration flask. Potassium hydroxide may be trapped, resulting in high saponification values.

Another obvious deterrent to the obtaining of theoretical saponification values is the relatively low boiling point of the ethyl alcohol. The rate of most chemical reactions is doubled or tripled for every 10°C. increase in temperature, and some reaction rates may even be increased six-fold for a 10°C. temperature rise. In order to increase the rate of the saponification reaction, a higher boiling solvent can be used or the lower boiling solvent can be employed under conditions of increased pressure in an autoclave or a sealed strong-walled tube. For a simple routine method it is preferable to use a higher boiling solvent to increase the reaction temperature.

Experimental

A number of various solvent systems were studied, including n-butyl alcohol, n-butyl alcohol-pyridine, n-butyl alcohol-benzene, ethyl alcohol-benzene, ethyl alcohol-n-butyl alcohol, and diethylene glycol. Preliminary results indicated that the systems utilizing n-butyl alcohol and ethyl alcohol-pyridine as the solvents gave the best results with the least complications, and further work was concentrated on those systems.

The methods employed in this work are all similar to the A.O.C.S. Tentative Method Ka 8-48 (9) with respect to alkali concentration and relative sample weights. Solvents were added to or replaced the ethyl alcohol in an attempt completely to dissolve the sample and to keep it in a homogeneous condition throughout the reaction. All results are reported on a 100% non-volatile basis.

Preliminary work indicated that the reagent grade of n-butyl alcohol was of sufficient purity as obtained. Potassium hydroxide is readily soluble at room temperature in n-butyl alcohol in the required concentration of 40 g. per liter. This solution is colorless and, on standing over a period of two or three weeks, will yellow but not sufficiently to affect use of the reagent. Determinations were made first at steam bath temperatures and finally at gentle reflux temperature of the reactants, using a variable heat control hot plate. Initial results were low, indicating incomplete saponification. It was found that, by addition to the reaction mixture of 1 ml. of water corresponding to approximately 5%, the resultant saponification values more nearly approached the theoretical.

TABLE I

Saponification Values of a Maleic Modified Tall Oil P. E. Alkyd in Butyl Alcoholic Alkali

	Reflux temperatures	Steam-bath temperatures
Theoretical value	212.2	212.2
Butyl alcohol, 1 hr.	157.5	......
Butyl alcohol, 2 hr.	187.2	......
Butyl alcohol + 2½% H_2O, 2 hr.	188.9	......
Butyl alcohol + 5% H_2O, 2 hr.	208.7	202.0

Table I illustrates the beneficial effect of water addition and also the increase in saponification value with an increase in temperature. As will be noticed, the observed saponification value of 208.7 does not agree with the calculated saponification value of 212.2. The sample used for illustration was a maleic-modified tall oil pentaerythritol alkyd, which gave an average sponification value of 163.9 in repeated determinations, using ethyl alcohol as a solvent. In the preparation of materials, such as this tall oil pentaerythritol maleic alkyd, there is possibility for some thermal cracking and loss of saponifiable constituents. In addition, some resinous insoluble components separate during preparation, resulting in variable and unknown changes in saponifiable material in the liquid phase. As a result, the saponification value calculated from the original reaction mixture is essentially an approximation. However the comparison of the calculated saponification value of 212.2 with the 208.7 and 163.9 values obtained, using butyl and ethyl alcoholic systems, respectively, illustrates the striking advantage of the higher alcohol.

In an effort to avoid uncertainties regarding composition caused by separation of resinous components during the preparation of maleic-modified oils, a simple maleic-modified control ester was prepared. A sample of dibutyl maleate of composition 70% fumarate and 30% maleate was reacted with methyl esters of linseed oil at a temperature of 240°C., using special precautions to avoid losses during heat processing. A material balance check indicated quantitative recovery. Based upon the starting composition of 43.6 parts of the maleate ester and 56.4 parts of the linseed methyl ester, the product corresponds to a 33.2% maleic anhydride modification of the linseed methyl esters. This represents a much higher degree of modification than can be obtained in normal oil processing. Saponification was carried out on the individual reactants, the simple blend, and the reaction mixture, using both ethyl and n-butyl alcohol systems.

TABLE II

Saponification Values of Maleic Modified Linseed Methyl Esters

Compounds	Theoretical sap. value	Solvent media	
		Ethyl alcohol	Butyl alcohol
Dibutyl maleate	493	481.1	494.5
Linseed methyl esters	193-197	194.2	194.5
Mixture before reaction	324	324.7	325.5
Mixture after reaction	324	284.6	326.2

Table II illustrates quite conclusively that butyl alcohol as a solvent for the saponification value determination of oils of the maleic-modified type gives results equivalent to the calculated values within experimental error. The inadequacy of ethyl alcohol is strikingly apparent.

A time *vs.* saponification value study was made on a series of four oils, comparing the rate of saponification in n-butyl and in the standard ethyl alcohol.

The four oils graphically represented in Figure 1 are as follows: a soybean oil-dicyclopentadiene copolymer, ordinary refined linseed oil, the previously described dibutyl maleate adduct with linseed methyl esters, and a maleic-modified tall oil pentaerythritol alkyd. Saponification values were calculated from the values for the reactants, taking into account the observed losses during processing.

It is evident that the rate of saponification in n-butyl alcohol is much greater than the rate of saponification in ethyl alcohol. It is also apparent that the butyl alcoholic saponification gives results in good agreement with the calculated saponification value for samples which are difficultly saponifiable in ethyl alcohol.

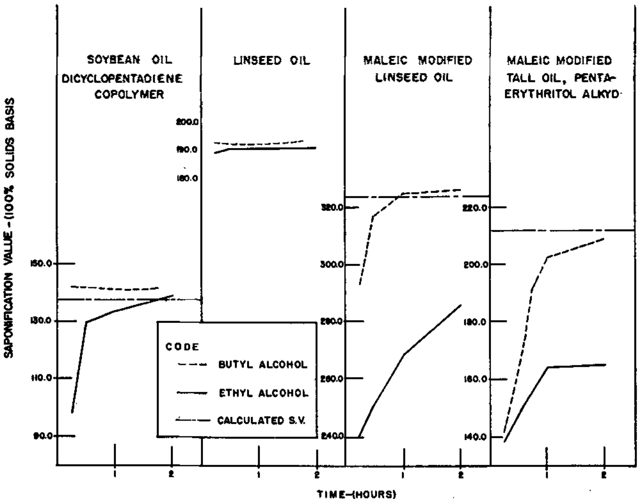

Fig. 1. Time *vs.* saponification value of ethyl alcohol-butyl alcohol solvent systems.

A homogeneous reaction is really the crux to the obtaining of "true" saponification values of drying oil products. On this basis it was thought that simple addition of a good fat solvent to the reaction flask containing the sample and the ethyl alcoholic alkali would give more nearly acceptable results. Pyridine was selected as a very good fat solvent with the added attractiveness of being miscible with water. After weighing the sample into the saponification flask, 25 ml. of reagent grade pyridine were added to dissolve the oil, ethyl alcoholic alkali was pipetted in, and saponification was carried out on the steam bath for two hours.

TABLE III
Saponification Values of Oils Using Three Different Solvent Systems

Oil	Theoretical	Ethanol		Ethanol-pyridine		n-Butyl alcohol	
		1 hr.	2 hr.	1 hr.	2 hr.	1 hr.	2 hr.
Refined linseed oil	189-192	......	190.1	......	191.9	......	191.9
Maleic modified linseed oil	238.2	......	231.5	......	236.1	......	234.0
Soybean dicyclo. copolymer	138.0	......	133.4	......	142.1	......	142.0
Maleic modified soybean oil	219.1	......	216.1	......	221.1	......	222.4
S/B glycerol alkyd dicyclo. copolymer	243.0	242.8	......	240.4	......	240.3	......
Soybean dicyclo. copolymer	142.0	144.6	......	146.8	......	145.4	......
Styrenated fish oil	119.0	109.7	......	124.2	......	123.0	......
Styrenated fish oil	109.0	78.2	......	113.2	......	113.3	......

In Table III the saponification values of a refined linseed oil, a maleic-modified linseed oil, a soybean dicyclopentadiene copolymer, and a maleic-modified soybean oil have been compared, utilizing ethyl alcohol, ethyl alcohol-pyridine, and n-butyl alcohol-5% water solvent systems. It can be seen that excellent agreement is possible on these types of oils, using either an ethyl alcohol-pyridine or an n-butyl alcohol solvent system for their saponification. In contrast, certain products give lower results, using the ethyl alcohol-pyridine system. For instance, the dibutyl maleate adduct of linseed methyl esters gave an average saponification value of 317.0 in duplicate determinations compared with the theoretical value of 324.0 and the n-butyl alcohol result of 326.2.

To this point the majority of the data have been concerned with the saponification of maleic-modified oils. The applicability of n-butyl alcohol and ethyl alcohol-pyridine solvent systems was tested for saponification of other types of chemically modified drying oils.

Table III also lists saponification values of two soybean oil dicyclopentadiene copolymers and two styrenated fish oils, using the three solvent systems described above. The approximate theoretical saponification values were calculated for these copolymer oils from the observed conversion of monomer to polymer in the preparation of these modified products. Such calculations are only approximate. It is apparent that the standard ethyl alcoholic alkali is entirely adequate for the dicyclopentadiene modified products. For the styrenated oils however the inadequacy of the standard solvent system of ethyl alcohol is apparent. The results by the n-butyl alcohol and ethyl alcohol-pyridine solvent systems are in very good agreement with each other and are reasonably close to the approximate theoretical values.

The detailed n-butyl alcohol saponification procedure developed in this work is described below in A.O.C.S. Methods format.

Saponification Value

Definition: The saponification value is a measure of the alkali reactive groups in fats and oils and is expressed as the number of milligrams of potassium hydroxide which react with 1 g. of the sample.

Scope: Applicable to natural and chemically modified drying oils.

A. Apparatus:

1. Erlenmeyer flasks, Corning alkali resistant, Kimble resistant or equivalent, 250 or 300 ml.
2. Air condensers, minimum 650 mm. long.
3. Hot plate with variable heat control.

B. Solutions:

1. Hydrochloric acid, 0.5N, accurately standardized.
2. n-Butyl alcoholic potassium hydroxide. Dissolve 40 g. of potassium hydroxide, low in carbonate, in 1 liter of n-butyl alcohol, keeping temperature below 25°C. while the alkali is being dissolved. This solution should be stored in an amber bottle.
3. Phenolphthalein indicator soln., 1% in 95% ethyl alcohol.

C. Procedure:

1. Weigh a sample of such size that the back titration is 45 to 55% of the blank. This is usually *ca.* 2 g. Add 25 ml. of the n-butyl alcoholic KOH with a pipet and allow the pipet to drain for a definite period of time. Add 1 ml. of distilled water.
2. Prepare and conduct blank determinations simultaneously with the sample and similar in all respects.
3. Connect the air condensers, and boil gently, but steadily until the sample is completely saponified. This usually requires *ca.* 30 minutes for normal drying oils. Certain chemically modified drying oils may require 1- to 2-hour heating periods. Be careful that the vapor ring does not rise to the top of the condenser, or there may be some loss.
4. After the flask and condenser have cooled somewhat, wash down the inside of the condenser with a little 95% ethyl alcohol. Disconnect the condenser and add sufficient ethyl alcohol to make the total amount added *ca.* 50 ml. Add *ca.* 1 ml. of indicator and titrate with 0.5N HCl until the pink color has just disappeared.

D. Calculation:

$$\text{Saponification value} = \frac{56.1 \times \text{N HCl (titration of blank} - \text{titration of sample)}}{\text{Weight of sample}}$$

Discussion of Results

Several different procedures have been checked for the saponification of a series of representative, difficultly saponifiable drying oil products. The inadequacy of the standard ethyl alcoholic alkali has been demonstrated quite conclusively, and it was shown that n-butyl alcohol-water and ethyl alcohol-pyridine solvent systems gave results in much better agreement with the calculated saponification value.

n-Butyl alcohol as a solvent for saponification of drying oil products offers definite advantages over the standard ethyl alcohol.

a) It is a much better fat solvent and gives homogeneous reaction conditions in most saponifications.
b) The reflux temperature of the 95% n-butyl alcohol-5% water mixture is approximately 40°C. higher than the reflux temperature of ethyl alcohol, and the saponification will thus proceed at a much faster rate, as shown in Figure 1. Based upon the empirical observation that reaction rates increase approximately two- or three-fold for each 10°C. rise in temperature, the butyl alcoholic saponification would be expected to be from 16 to 81 times as fast as in the ethyl alcohol system.
c) Because of the higher boiling point of n-butyl alcohol, a higher boiling ester results from alcoholysis, which minimizes the possibility of loss of volatile saponifiable material.

There is one glaring disadvantage encountered in using n-butyl alcohol. The determination of the endpoint is very difficult when using phenolphthalein as the indicator in the titration of the excess alkali with hydrochloric acid in contrast to the fairly good end-point in the ethyl alcohol or the ethyl alcohol-pyridine systems. Potentiometric titrations were made for the systems of ethyl alcohol-water, n-butyl alcohol-water, and n-butyl alcohol-ethyl alcohol-water.

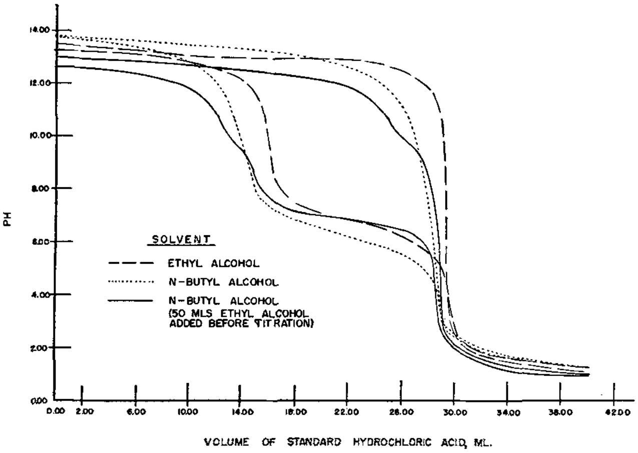

FIG. 2. Titration graph of saponified linseed oil.

In alcohol systems the pH is only a relative term; however it is a repeatable measurement even if not a "true" one. The slope at the end-point for the blank in the ethyl alcohol-solvent system represented by the broken-line curve in Figure 2 is 0.037 and for the sample of the saponified linseed oil at the phenolphthalein end-point the slope is 0.308. The normal good break in the curve when titrating a strong base with a strong acid is observed. The curve is flatter and covers a much narrower pH range in the titration of the salt of the weak acid obtained by saponification.

Figure 2 adequately explains the difficulty in obtaining a precise end-point with an indicator in the n-butyl alcohol system. The solid line curve for the blank depicts titration of n-butyl alcoholic alkali in water with aqueous hydrochloric acid. The peculiar hump near the end-point is rather disturbing, and no adequate explanation is available. Possibly the inflection could be caused by the immiscibility of butyl alcohol and water in that at the breaking point or end-point the last traces of free potassium hydroxide have to be extracted by the water from the butyl alcohol. This may be a slow process, causing the indicator to fade and at the same time causing the pH to change only slightly on addition of acid. It was thought that this condition could be corrected by the simple addition of a water-butyl alcohol miscible solvent such as ethyl alcohol. By inspection of the dotted-line curve it can be seen that this was partially accomplished. However the results, though corrected somewhat, leave much to be desired as the slope for the blank is 0.282 and for the sample, 0.658. Compared to the obtained slopes of 0.037 and 0.308, using ethyl alcohol-water as titration media, it can be readily seen that a relatively slight error in titration could cause appreciable errors in the results.

Conclusions

The use of n-butyl alcohol as a solvent for saponification of a representative series of drying oils has been studied. It appears from this work that n-butyl alcoholic potassium hydroxide reagent, containing 5% of water added to the reaction mixture, gives very acceptable results based upon calculated saponification values.

With the exception of maleic-modified oils of certain types, the solvent system of ethyl alcohol-pyridine exhibits excellent results based upon calculated values. However it has the disadvantages that it is a two-solvent system, and the pyridine must be of reagent grade to avoid end-point difficulties.

The end-point in the butyl alcohol system is not as sharp as the normal saponification end-point in ethyl alcohol. This may be caused by the two-phase nature of the titration mixture. Addition of ethyl alcohol to the n-butyl alcoholic saponification reaction mixture gives improvement, although the end-point is not as sharp as in the regular ethyl alcohol system. Work is continuing on methods for improvement of the end-point.

REFERENCES

1. Shaefer, W. E., and Balling, W. J., Anal. Chem., *23*, 1126 (1951).
2. Shaefer, W. E., and Piccard, J., Ind. Eng. Chem., Anal. Ed., *10*, 515 (1938).
3. Pardee, A. M., and Reid, E. E., J. Ind. Eng. Chem., *12*, 129-33 (1920).
4. Henriques, Ann., *120*, 351 (1861).
5. Bertoni, Gazz. ital., *12*, 435 (1882).
6. Reid, E. E., Am. Chem. J., *45*, 506 (1911).
7. Anderson, Ernest, and Pierce, H. B., J. Phys. Chem., *22*, 44 (1918).
8. Pardee, A. M., Hasche, R. L., and Reid, E. E., J. Ind. Eng. Chem., *12*, 481-2 (1920).
9. Official and Tentative Methods of the Am. Oil Chemists' Soc., 2nd edition, Section K.

[Received March 2, 1954]

Simultaneous Recovery of Wax and Oil From Rice Bran by Filtration-Extraction[1]

JOSEPH POMINSKI, P. H. EAVES, H. L. E. VIX, and E. A. GASTROCK, Southern Regional Research Laboratory,[2] New Orleans, Louisiana

MANUFACTURERS of wax preparations for home and industrial uses in this country are interested in obtaining new sources of hard vegetable waxes other than carnauba. For the year 1951 the United States imported 26,340,000 pounds of vegetable waxes valued at $21,082,000, the largest part being carnauba, 16,016,279 pounds worth an average price of $0.929 per pound (11). Potentially rice bran is a source of hard vegetable wax. Rice bran contains a percentage range of lipids which are about 14 to 17% oil (8) of which 3 to 9% is wax. The yield of the total available lipids and the oil-wax relationship will be dependent upon the solvent temperature

---

[1] Presented at the annual fall meeting, American Oil Chemists' Society, Nov. 2-4, 1953, Chicago, Ill.

[2] One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, United States Department of Agriculture.