Accelerated Aging Tests for Soap*

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INTRODUCTION

THE problem of spoilage in commercial soaps through alterations in color and odor and by chemical changes which are distinguished collectively as "rancidity" has probably existed as long as soap making has constituted an industry. Among the factors which no doubt did much to focus attention on the importance of stability in soap may be included the advent of the commercial laundry with its large requirements for quickly soluble concentrated bulk soap chips and flakes of 88% anhydrous soap content. In addition, white flakes intended for fine laundering purposes in the home must be free from the slightest trace of rancidity and the manufacture and national distribution of package products of this type has necessitated rigid control of production methods.

No longer ago than 1920 prominent manufacturers of 88% soap chips suffered serious losses of product and consumer confidence through deterioration of material, for which an adequate explanation was frequently difficult at that time. Rancid soap lacked body in the laundry wheel, and in addition imparted a sharp disagreeable odor which persisted on the finished goods. Textile soaps have been subject to the same problem, and in the silk industry the decrease in degumming power of soap which has suffered oxidation is well known (1). Toilet soaps, commonly produced in white or light-colored shades, have a longer average life from manufacture to final use, and are consumed more slowly during use, than other soap products. Discoloration and spotting, with or without alteration of odor, has been at one time or another a matter of concern to the industry.

Almost immediately after the recognition of stability or resistance

to spoilage as a major technical problem of the soap industry, chemical research was undertaken in various quarters with the three-fold purpose of (1) determining the causes of spoilage (2) discovering means to prevent deterioration and (3) devising methods for predicting the stability of freshly-made soap. The literature of the past decade indicates something of the large amount of work and the number of investigators devoted to these first two objectives. A discussion of these phases of the stability problem, however interesting and closely related to accelerated aging tests, is clearly beyond the scope of the present notes. Our object at this time is to describe a few simple procedures for the accelerated aging of soap which have gained more or less currency in the industry. Excluded from present consideration are the many tests for stability of fats and oils, the relation of which to soap stability seem probable but not yet conclusive.

Very little has appeared in the literature on the prediction of soap stability by accelerated aging. The present authors are undertaking to report something of their experience and ideas in the hope that the subject may be opened more fully for discussion. For this reason it seems appropriate to outline briefly the authors' concepts of the mechanism of spoilage in soap which have led to the adoption of certain tentative aging tests to be described herein.

Mechanism of Spoilage

The deterioration of soap is held to be due chiefly to either or both of two causes, oxidation and hydrolysis. Rancidity is understood to mean a special form of spoilage involving the formation of free fatty acid, and one or more by-products, the nature of which vary from case to case, and have not been fully identified in general.

Nicolet and Liddle (2) indicate that the common eighteen-carbon unsaturated fatty acids tend on oxidation to split at the central double bond with the formation in part of dibasic azelaic acid; that this product may exist as a semi-glyceride, perhaps trisemiazelain and mixed glycerides; and that by-products appear to include aldehydes etc. Highly rancid cottonseed oil contained as high as 10 per cent of azelaic acid or a glyceride of this acid. A shredded laundry soap which had developed 2 per cent of free acid on storage contained about 0.5 per cent azelaic acid.

Smith and Wood (3) investigated the accelerated aging of soaps in a moist atmosphere at 100° F. for periods up to 40 weeks, following deterioration by observing relative color changes with a Hess-Ives tint photometer. They found that the rate of increase of color conformed to typical rates of oxidation of organic substances. Silman (4) reports rancidity to be chiefly the consequence of oxidation processes; catalyzed, especially in sunlight, by traces of metals of which the most important are copper, cobalt, and iron; and facilitated in solution as compared with behavior in solid soap. King, Roschen, and Irwin (5) found that peroxide formation in oils and fats, paralleling rancidification, was accelerated most by copper on a list of metals apt to be encountered in plant operation. Emery and Henley (6) found that air, light, and metals are among the factors that influence rancidity, and are more important than moisture. The indications of a photochemical oxidation mechanism are confirmed by Coe (7), in one of the most extensive investigations on the mechanism of rancidity reported in the recent literature, who concludes among other things that unsaturated triglycerides may undergo peroxide formation, which in turn split into aldehydes and unidentified components of the

rancid compound. Bailey (8) in his excellent book concludes that "rancidity presumably depends, not merely on the fat being oxidized, but on its being oxidized to particular compounds."

A method that has been contemplated for some time by the present authors involves following the oxygen absorption of a sample of soap having a known surface area and depth, maintained in a closed system at constant temperature, by means of a mercury manometer having an automatic leveling device to keep the total pressure constant. Wright and Mills (9) investigated the rate of isothermal oxygen absorption of lubricating greases by means of a closed absorption bomb, operating at initial oxygen pressures of 110 pounds per square inch absolute over a temperature range of 175° — 245° F. The greases used contained from 11 to 28% sodium soap. Effect of metallic impurities and of inhibitors was studied, and rate curves were obtained of oxygen absorption vs. time having typical S-shapes with an initial induction period.

Applying the concept of atmospheric oxidation of unsaturated fatty acids as the main cause of rancidification to a bar of soap such as toilet soap, it follows logically that deterioration begins on the surface. If the surface layer of a rancid bar is carefully shaved off and compared with the interior of the same bar, a higher acid content is found in the exterior portion and the color is usually though not necessarily darker. If minute inclusions of metallic particles, such as copper, brass, or iron exist in the soap, visible evidence usually develops as to their role in accelerating deterioration. Other variables which affect the rate of oxidation include the moisture content of the soap, the content and character of any unsaponified and unsaponifiable matter, the total and free alkali, and the surface area exposed to the air. Aging tests, to be comparable, need to eliminate one or more of these variables.

Origin of the Film Test

One of the authors devised a test some years ago in the laboratory of another organization which sufficed to indicate the relative stability of soap with respect to oxidative rancidity. The test was based on the premise that if two

samples of soap could be reduced to the same low moisture content, with surface areas per unit of weight substantially equivalent, and if the surface exposed to oxidation could be extended to a degree such that oxygen could penetrate through the entire mass, rancidification could be rapidly induced upon exposure of the samples to humidified atmosphere at elevated temperature.

Reduction of the soap to a uniform surface area and thickness is accomplished by dissolving a standard quantity in warm water sufficient to form a gel on cooling in a flat mold of large cross section. The gel is transferred to a drying screen of non-corrosive alloy metal and dried to yield a thin soap film. The film is removed, weighed into a glass jar, sealed under controlled humidity, and maintained in a thermostat oven for a period of hours or days, usually 72 hours. The original soap solution having been carefully neutralized, subsequent deterioration is evaluated by determining the free acid in the aged film. This method has been used in some form for over 15 years, and has evolved in the hands of the originator, R. E. Divine, into the procedure described below.

On behalf of the method it may be said that it provides an aging condition conducive to a high rate of deterioration, particularly of the oxidation type. Tendencies to spoilage as a consequence of incomplete saponification, peroxide formation, or other loosely-held oxygen of combination, traces of copper or other metallic catalysts, or unsaturation of an especially vulnerable sort, are very apt to manifest themselves in the course of this test. A fair correlation exists between the results of this test and other accelerated aging tests, and most importantly, with one-year normal aging. The test is capable of reasonably quantitative expression in terms of units of alkali per unit of anhydrous soap, as well as the usual qualitative grading on the basis of color and odor.

Among the limitations which the authors recognize — and there are undoubtedly others — may be mentioned the sensitiveness of an aging test accelerated to the 72-hour period normally employed. Small differences between two samples, even of supposedly identical soap, may

become magnified in the course of this test to a disproportionate extent. Duplicate determinations made with the greatest care will not always develop identical rancidity, and while the deviation from the mean averages about ±5%, occasionally larger deviations are obtained. Aside from color and odor appraisal, the quantitative feature of the test depends upon the titration of free fatty acid. It is not certain that what is called rancidity can always be properly evaluated in terms of free acid. As between samples of similar soaps made from the same stocks, but perhaps differing only in age, number of washes, time of settling, temperature of dryer, or other incidental processing, free acid as developed in this 72-hour aging test has proved to be a surprisingly good index of relative stability.

Attempts to compare soaps of different origin or different stocks usually lead to anomalous results. As pointed out by Bailey, rancidity depends, not merely on the fat being oxidized, but on its being oxidized to particular compounds. Within these limitations, the 72-hour test has proved of definite value in enabling prompt comparisons to be made between similar lots of soap, relative to some standard already determined by correlation with one-year normal aging tests (i.e., conditions paralleling shelf or window storage within temperature and humidity ranges normal to a 12-months period).

Need for Further Work

In conclusion the authors wish to state that in presenting these tentative procedures for accelerated aging of soap, they do so largely in the hope that constructive criticism will follow, leading to the development of more satisfactory tests. It has been their experience that no one accelerated test by itself may be relied upon to predict the degree of long-time stability, but that by using several of these tentative methods, a composite estimate may be obtained which is quite helpful. Some of the tests, including the 72-hour film test, tend to impose more severe conditions than the soap is likely to encounter in its normal life, and discoloration may be obtained in oven tests to an extent rarely paralleled in prac-

tice. Such tests are valuable, however, in bringing out differences.

An extremely interesting field in which conclusive evidence is lacking is the relation of stability of fats and oils to the stability of the soap made from them. Powell (10) reveals an apparently strong interdependence which, if more fully explored, could prove of great value to the soap industry.

ACCELERATED AGING

TESTS

HOOKER SOAP

LABORATORY

The general experience of laboratories in the soap industry who have used accelerated aging tests of any sort has been that these tests are only qualitative, and usually do not show up minor differences. They generally permit one to distinguish between a piece of soap that will go "off" and one that will remain stable, and are based on a normal age of one year. They are usually "relative" tests and must be made with reference to a "control" sample to be significant.

I. Three-day Film Test

This test is more rapid than the bar test, therefore more sensitive, and is a chemical test permitting rather quantitative evaluation of "stability." It is based on the concept of the spoilage of soap as being due to atmospheric oxidation, with oxidation products causing darkening, and eventually developing free fatty acid, aldehydes, and ketones, which give rise to odor. Due to the different ways in which different soaps will change, this three-day test method is more significant when used to distinguish between soaps made from the same stock.

Since atmospheric oxidation is a

*Note: It may be desirable occasionally to compare relative stabilities of soaps containing free alkali in some form. In such cases the soap may be still alkaline after 72 hours exposure, and in such case the titration is made with N/4 HCl.

surface effect, this method is chiefly a technique for converting the soap into film form.

Dissolve 15 grams of soap in 150 ml. distilled water by heating on steam bath until clear. Neutralize exactly by adding N/4 HCl in amount found necessary by separate test for free alkali.* (This step insures that all samples of soap are started off from a common point, and avoids advantages or handicaps in stability otherwise arising from content of free alkali.)

Pour the clear soap solution onto a leveled glass plate and allow to cool until gelled. Chill a few minutes in a refrigerator. Transfer to a wire screen and dry overnight or longer if necessary. Every precaution must be taken to keep the sample clean and to avoid contamination with metals, especially copper and iron. Where fairly frequent use is made of this three-day test, it is convenient to have 12 each of the glass plates and wire screens on hand, and a rack for the screens while films are drying.

Glass Plate

Ordinary window glass is cut 13" x 15", and a retaining edge is provided by glueing on flat strips of glass one-half inch wide around the sides of the plate. This provides a liquid depth equal to the thickness of glass used. Ordinary animal glue has been found superior to all other cements for present purposes. The plate should be washed with alcohol not water. Before pouring the soap solution onto it, it should be carefully leveled with a spirit level to provide a soap film of uniform thickness.

Wire Screen

The gelatinous soap film is transferred to a drying screen by inverting the glass plate and "teasing" the film off onto the screen with a spatula. If one end of the film is loosened and placed in contact with the screen, the remainder will readily drop in place. The screen consists of a piece of 18 mesh aluminum screen cut 15" x 20", mounted on a light wooden frame similar to a window screen. The frame consists of ¾" x 1½" strip, assembled to give a frame 1½" thick. The screen is cleaned with a stiff brush, no water being used.

Remove the dry soap film from the screen, weigh, and transfer the flakes to a one pint Mason jar. Roll

an 18½ cm. filter tightly on a glass rod, slip off rod, bend double at center, and measure 1½ ml. water, placing half on each limb of the filter. Place this in the jar with the soap film, close tightly with cap and rubber band. Place in a thermostat oven at 105° F. for 72 hours. Remove from oven, take out filter paper, add 150 ml. benzol alcohol soap solvent, and heat on water bath until soap is dissolved. Cool, add phenolphthalein and titrate with N/4 NaOH (aqueous solution). The quantity of alkali solution required to neutralize the acidity developed in ten grams of soap is taken as a measure of stability, relative to another sample of some similar soap.

Odor and color of films should be noted each day while films are in oven. Color, odor, and acidity form the basis of judging the stability of the soap under test.

Benzol-alcohol Soap Solvent

This is the solvent recommended by Uhlig and Duemmling (OIL & SOAP, December 1936) and avoids hydrolysis of the soap and inaccurate end point. It consists of 70 parts of benzol and 30 parts of 95% ethyl alcohol. The solvent should be brought to exact neutrality before use.

II Nine-day Bar Test, 140°F

Maintain an unwrapped bar of soap in a thermostat oven at 140° F. exposed to air for nine days. The soap will dry, and may at the same time develop color or odor.
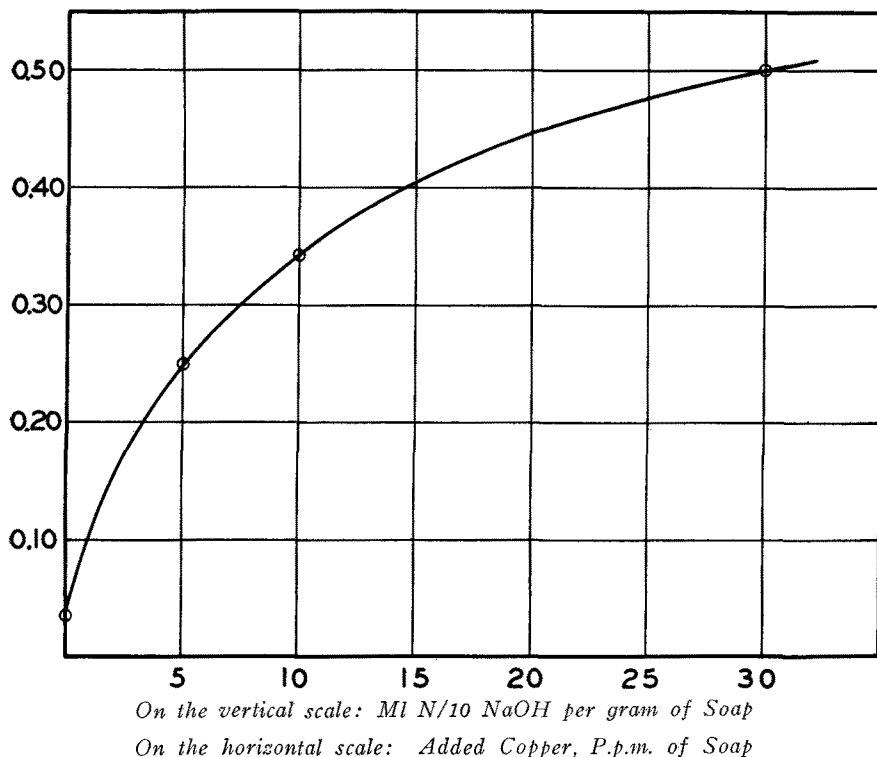
The exposed bar is observed for color and odor.

III 125°F Open Oven Test

Bars of milled or floating soap are placed on a glass plate exposed to the air inside a thermostat oven at 125° F. for 6 weeks. Due to drying out of the soap this test may not be as severe as the 125° F. sealed jar test (No. V), but is recommended as giving useful information on direct atmospheric oxidation.

IV 100°F Sealed Jar Test

This is similar to the 125° F. test except that it is designed for kettle soap or similar products for which 125° F. is apt to be too high. Kettle soap cut into bars is placed in

Title: *Fig. I. Effect of Minute Amounts of Copper in Accelerating Rancidification of Soap*

On the vertical scale: Ml N/10 NaOH per gram of Soap

On the horizontal scale: Added Copper, P.p.m. of Soap

sealed jars in an oven at 100° F. for 6 weeks.

V 125°F Sealed Jar Test

Soap in the form of milled bars, white floating cakes, cakes from the dryer, or chips from the mill, is placed in a clean dry fruit jar of one pint size equipped with rubber ring and tight cover. (The sample should be supported on glass so as to be above the bottom of the jar, where moisture collects). The covered jar is placed in a thermostat oven at 125° F. for a period of weeks. Normally 6 weeks (42 days) is found to represent at least one year of normal aging. The soap is graded for color and odor at the start and finish of the test, but preferably is not disturbed during the test.

VI Ultraviolet or Sunlight Stability

Samples of soap in bar or other form are exposed to all available sunlight during a period of four weeks. Preferably the cakes are not disturbed, in order to permit comparison with the unexposed portions, as well as with other samples.

An improved procedure as used in the Hooker Laboratories is to expose the soap at a distance of 24 inches from an ultraviolet mercury vapor lamp in a cabinet under conditions where no heating occurs. Exposure for 4, 8, or 12 hours is usually sufficient to develop any instability toward sunlight.

Grading of Samples in Accelerated Tests

The grading of soap samples should be done by experienced persons if the results are to be significant. Even then it has been found very desirable for the same observer to repeat his grading several times and strike an average, without reference to the code number on the sample until his selection is completed. Color grading by eye should be done if possible under a "daylight" lamp in a dark room free from reflected light; otherwise under a north light where the samples all have equal illumination. Experienced color graders have found that they cannot judge effectively for more than twenty minutes at a time. For accurate grading of color free from the human equation, a recording spectrophotometer (as manufactured by the General Electric Co., Schenectady, N. Y.) is the most satisfactory instrument.

In coding the samples, statistical studies on identical items have shown a tendency to pick "No. 1" over "No. 2", or "A" instead of "B", or vice versa, merely from association, or from an effort to resist association. Preferred practice is therefore to use random numbers of four figures such as 3627, 5128, 4592, etc.

EXPERIMENTAL RESULTS

Typical results of relative stability tests using the 3-day film procedure described above are presented in adjoining tables. In Table I, triplicate determinations were made on two samples of toilet soap base identical in every respect except for a special treatment accorded the first sample. The average deviation from the mean is ± 2.8%. The untreated second sample developed deeper color and 30% more free acid than the first sample.

In Table II the ability of the method to discriminate between various stabilizers is demonstrated. This series was kept in the oven for 96 hours. Again samples were run in triplicate to provide fuller information on reproducibility of results, although normal practice is limited to duplicate determinations. All of the four samples represented in this table are from the same frame of soap, differing only in the nature of the addition compound. As the acidity developed under identical conditions falls from 4.97 ml. N/10 NaOH per 10 grams soap to a value of 2.03 ml, the color improves from very light cream to very white and the odor from rancid to sweet.

Soaps having different origins may not be comparable by the 3-day film test for relative stability. Table III shows that Kettles 10, 11, and 12 of similar type gave results averaging about 10 ml; Sample 4157 developed only about one-half this acidity after exposure to the same conditions, while samples 4158 and 4159 developed still less. In this series, the degree of rancidity apparent to sense of sight or smell was not directly correlated with the developed acidity; that is, between soaps of very different origins, the film test in its present form does not give a figure which has any 'absolute' value. Perhaps this will be possible when rancidity can be defined quantitatively.

TABLE I
3-DAY FILM TEST — TYPICAL RESULTS ON TOILET SOAPS

Sample No.	Odor	Color	Acidity Ml. N/10 NaOH	Per Cent Deviation
Treated Caustic				
71138—A	S	Cr W	2.20	4.3
—B	S	Cr W	2.10	0.5
—C	S	Cr W	2.04	3.3
Mean			2.11	
Untreated Caustic				
71138—A	S	Cr Y	2.74	0.4
—B	S	Cr Y	2.87	4.3
—C	S	Cr Y	2.64	4.0
Mean			2.75	

Average Deviation, % ± 2.8

Note: S = Sweet
N = Neutral
FR = Faintly Rancid
R = Rancid

VW = Very White
W = White
Cr = Cream
L = Light
Y = Yellow

TABLE II
FILM TEST — TYPICAL RESULTS SHOWING EFFECT OF STABILIZERS ON TOILET BASE
(Note: This Series in Oven for 96 Hours)

Sample No.	Odor	Color	Acidity Ml. N/10 NaOH	Per Cent Deviation
K 38—A	R	W	5.28	6.2
—B	R	V L Cr	5.28	6.2
—C	FR	V L Cr	4.36	12.3
Mean			4.97	
K 38+X—A	FR	W	2.82	6.8
—B	FR	W	2.53	4.2
—C	N	W	2.56	3.0
Mean			2.64	
K 38+Y—A	S	VW	2.03	6.9
—B	S	VW	2.03	6.9
—C	S	VW	2.48	13.8
Mean			2.18	
K 38+X +Y—A	S	VW	2.03	0
—B	S	VW	1.95	4.0
—C	S	VW	2.10	4.0
Mean			2.03	

Average Deviation, % ± 6.2

TABLE III
3-DAY FILM TESTS — ACIDITY DEVELOPED IN SOAPS OF DIFFERENT HISTORIES
Acidity Ml. N/10 NaOH

Sample No.	"A"	"B"	Mean	% Deviation
K 10	10.63	9.39	10.01	6.2
K 11	10.86	12.14	11.50	5.6
K 12	9.18	8.50	8.84	3.9
4157	5.30	5.30	5.30	0
4158	0.52	0.52	0.52	0
4159	2.13	1.90	2.01	5.5

Average Deviation, % ± 3.5

TABLE IV
3-DAY FILM TEST — EFFECT OF COPPER ON STABILITY
Acidity Ml. N/10 NaOH

Sample No.	Copper Added, ppm	"A"	"B"	Mean	% Dev'n
92936	none	0.4	0.4	0.4	0
92937	5	2.8	2.1	2.5	14
92938	10	3.3	3.5	3.4	2.9
92939	30	5.3	4.7	5.0	6.0

Average Deviation, % ± 5.6

TABLE V
WHITENESS OF TOILET SOAP BARS AND 3-DAY FILM TEST AFTER 3 MONTHS NORMAL AGING
Recording Spectrophotometer

Sample	Per Cent Yellow	Brightness	3-Day Test Acidity
3A	13.3	74.2	1.53
4A	13.9	74.8	1.57
CA	15.2	66.9	1.71
CD	17.5	69.8	1.90
DC	20.3	62.6	2.80
CB	22.7	61.4	2.94

Table IV reports the progressive decrease in stability attending the addition of increasing amounts of copper to a given soap base. Apparently it made no difference whether the copper was added in the form of the metal, inorganic salt, or a soap. It was equally harmful in any form, unlike iron which seems to be less harmful in its inorganic salts or free state. The same information is shown graphically in Figure 1, confirming the results of many investigators as to the relative harmfulness of as little as 2 p.p.m. of copper (as Cu).

Some question has existed as to the inter-relation of color and free acid in rancidification. Soaps may develop a rancid odor but at the same time acquire a lighter color (bleaching), especially in sunlight. Other soaps, such as varieties of old-fashioned pure olive-oil castile, may become quite brown with little or no odor or free acid. Table V indicates that a typical toilet soap base made from 80% tallow — 20% refined coconut oil, with or without the use of a pre-treated saponifying reagent, and with transfer of nigres in certain cases, develops yellow color and loses brightness in 3 months normal aging in direct proportion to the free acid developed in the 3-day film test. The film test data presented here were obtained at the expiration of three months normal aging. Samples 3A, 4A, and CA were prepared with the pre-treated saponifier, and are shown by the General Electric recording spectrophotometer to be lighter-colored than the other three samples, while the film test indicates better stability.

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