

The results are shown in Figure 7. In every case an increase in acid number from 0.185 to 2.89 lowered the oil absorption. The decrease was greatest in the case of zinc oxide and least with Titanox. Further increase in acidity to 6.07 further decreased the oil absorption with zinc oxide, lithopone, basic lead sulfate, and Titanox, but did not further change the value for electrolytic white lead and actually increased the oil absorption of Dutch process white lead. There seems to be a more or less general qualitative relationship between the effects of acidity on oil absorption and on yield point, an increase in yield point being usually associated with a decrease in oil absorption. The most marked exception is in the case of Titanox. With this pigment both the yield point and the oil absorption decreased with increase in acidity, although the effect on yield point was much more pronounced than that on oil absorption.

The acidity of the oil influenced, not only the amount of oil required to wet the pigment, but also the character of the paste obtained when the pigment was completely wetted. Usually the nearly neutral oil gave a paste which was somewhat friable and sandy, while the oil containing free acid gave smoother and creamier pastes. In the case of zinc oxide the addition of 22 drops of neutral oil in excess of that required to wet the pigment thinned the paste only slightly, while the same excess of oil of high acidity gave a thin paint.

Effect of Nature of Thinner on Plastic Characteristics of a Paint

Paints were prepared from zinc oxide, lithopone, and Dutch process white lead. In each case the vehicle used was linseed oil with an acid number of 0.185, the amount being just sufficient to give a rather thick paint. From each such base paint thinned paints were prepared by the addition of known amounts of pure gum turpentine, petroleum thinner, or xylene. The plastic characteristics of each base paint and of the three thinned paints prepared from it were measured. The results are shown in Table II.

Table II—Effect of Various Thinners on Plasticity of Paints Containing Different Pigments

THINNER	DUTCH PROCESS WHITE LEAD PAINT ^a		LITHOPONE PAINT ^b		ZINC OXIDE ^c	
	Yield point	Mobility	Yield point	Mobility	Yield point	Mobility
	Cm. Hg		Cm. Hg.		Cm. Hg	
None	9.5	0.105	27.5	0.065	26.4	0.055
Turpentine	7.1	0.18	13.7	0.25	17.5	0.18
Petroleum thinner	6.0	0.22	12.0	0.33	14.6	0.22
Xylene	6.0	0.24	12.0	0.34	14.6	0.23

^a Base paint made with 210 grams of pigment and 70 grams of oil. Thinners added in the ratio of 3.33 grams to 100 grams of the base paint.

^b Base paint made with 100 grams of pigment and 99.67 grams of oil. Thinners added in the ratio of 8.9 grams to 100 grams of the base paint.

^c Base paint made with 130 grams of pigment and 60.25 grams of oil. Thinners added in the ratio of 8 grams to 100 grams of the base paint.

In every case the effect of turpentine in lowering the yield point and in increasing the mobility was much less pronounced than that of either the petroleum thinner or the xylene. The lower efficiency of turpentine as a thinner is probably related to its tendency to cause agglomeration of the pigment.

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Some Unusual Alcoholic Fermentations¹

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THE quantities of alcohol that can be produced in fruit juices and other suitable solutions by yeast fermentation vary with the composition of the solution, the nature of the yeast, and the environment. In the normal commercial manufacture of wines it is a rare fermentation that will produce more than 16 per cent alcohol by volume, even if sufficient sugar were present in the must. Several years ago in California wines that contained more than 18 per cent alcohol by volume were made solely by fermentation, but in order to obtain such high concentration special treatment was necessary, such as repeated additions of sugar or concentrated grape must while the fermentation progressed. No authentic information has come to the writers' attention of a case where more than 18 per cent alcohol by volume has been produced by the unmolested fermentation of a must containing originally sufficient sugar for the purpose—i. e., normal fermentation.

In a former employment the senior author made many

unsuccessful attempts to ferment 18 per cent alcoholic wines in the normal way. He secured yeasts from many parts of the world and tried many different must compositions without avail. Correspondence with oenological and fermentation experts at home and abroad brought the unanimous opinion that no yeast could produce normally as high as 18 per cent alcohol in wine, for it would cease to function before this alcoholic strength was reached. Eoff worked solely with pasteurized grape musts at this time and, as will be shown later, the probable cause of his failure was his inability to obtain fresh must.

In the summer of 1925 the writers were interested in the development of some non-intoxicating beverages to which were added small amounts of different fermented fruit juices to obtain flavor. Among the fruit juices tried was fermented pineapple juice. A few fresh pineapples were secured and ground without peeling in a hand meat grinder. To 1 gallon of crushed pineapple were added 2.5 gallons of 35 per cent cane-sugar solution and a small quantity of active Tokay yeast, the whole being placed in a glass jar. After standing at room temperature for 24 hours, vigorous

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fermentation was manifest, and the juice was pressed off. About 3 gallons of juice was obtained, which was placed in gallon jugs plugged with cotton. The jugs were put in a room at 15° C. and were not disturbed for 44 days, at the end of which time fermentation had ceased. A product of considerable sweetness, little alcohol, and high flavor was anticipated. On the contrary, a pineapple wine of no sweetness, much alcohol, and no high flavor was found. Closely agreeing analyses showed the wine to contain 19.2 per cent alcohol by volume and 1.8 per cent sugar.

The pineapple fermentation was so unique that the experiment was repeated yearly as fresh pineapples appeared on the market, and only in one year (1928) was there failure to reach 19 per cent alcohol. Many other experiments were made in an effort to determine the controlling factors for such high alcohol yields, and the details of some of the tests are given herewith.

Description of Experiments

- 241—1 part crushed fresh pineapple and 2.5 parts 35° Brix sugar solution, inoculated with Tokay yeast. After 24 hours on pulp at room temperature, pressed, jugged, and stored at 15° C. for 44 days.
- 559—1 part 28° Brix solution of old concentrated grape must and 2 parts 30° Brix sugar solution inoculated with new strain Tokay yeast, jugged, and allowed to stand at room temperature for several months.
- 560—Same as 559, but inoculated with old strain of Tokay yeast.
- 561—Same as 559, but inoculated with a Mosel yeast.
- 562—Same as 559, but inoculated with a Steinberg yeast.
- 602—1 part of crushed fresh pineapple and 2 parts 35.5° Brix sugar solution, inoculated with old strain Tokay yeast. After 24 hours at room temperature, pressed, jugged, and stored in 15° C. room until fermentation ceased.
- 603—Same as 602, but kept at room temperature.
- 604—Same as 602, but reduced acidity by addition of potassium hydroxide.
- 605—Same as 602, but inoculated with new strain Tokay yeast.
- 606—Same as 605, but kept at room temperature.
- 607—Same as 604, but inoculated with new strain Tokay yeast.
- 608—Same as 602, but inoculated with Steinberg yeast.
- 609—Same as 603, but inoculated with Steinberg yeast.
- 610—Same as 604, but inoculated with Steinberg yeast.
- 611—Same as 605, but used solution of 36.8° Brix crystallized dextrose instead of cane-sugar solution.
- 612—Same as 611, but kept at room temperature.
- 613—Same as 611, but reduced acidity by addition of potassium hydroxide.
- 682—1 part crushed fresh Concord grapes and 2 parts 35.2° Brix cane-sugar solution inoculated with new strain Tokay yeast. After 24 hours at room temperature pressed from pulp, jugged, and placed in 15° C. room until fermentation ceased.
- 683—Same as 682, but kept at room temperature.
- 686—1 part fresh Concord grape juice and 2 parts 35.2° Brix cane-sugar solution, inoculated with new strain Tokay yeast. Placed immediately in 15° C. room, where it remained until fermentation ceased.
- 687—Fresh Concord grape juice fortified with cane sugar to 30° Brix, inoculated and fermented the same as 686.
- 688—Crushed fresh Concord grapes fortified with cane sugar sufficiently to produce 30 per cent sugar in the mash, inoculated with new strain Tokay yeast. After 24 hours pressed off, jugged, and placed in 15° C. room until fermentation ceased.
- 1037—1 part crushed fresh pineapple and 2 parts 36.7° Brix cane-sugar solution, inoculated with new strain Tokay yeast. After 24 hours at room temperature pressed off and jugged, then sterilized half-hour at 100° C., cooled, reinoculated with same yeast, and placed in 15° C. room until fermentation ceased.
- 1039—1 part crushed fresh pineapple and 2 parts 36.7° Brix cane-sugar solution, inoculated with new strain Tokay yeast. After 24 hours at room temperature pressed off, 0.05 per cent urea added to juice, jugged, and placed in 15° C. room until fermentation ceased.
- 1040—Same as 1039, but no urea added.
- 1042—Crushed fresh pineapple inoculated with new strain Tokay yeast, and juice pressed off after 24 hours. To 6000 cc. of juice added 2700 grams cane sugar and 500 cc. water and

little more yeast and placed in 15° C. room until fermentation ceased.

- 1043—Same as 1042, but added 0.05 per cent urea to pressed-off juice.
- 1044—Same as 1040, except that during fermentation jug was kept in room where temperature varied from 0° to 5° C.
- 1045—Same as 1040, except that during fermentation jug was kept in room where temperature was maintained at about 10° C.
- 1538—4 liters crushed fresh pineapple and 1150 grams cane sugar inoculated with new strain Tokay yeast propagated through 5 transplantings in sterilized grape must. After 24 hours at room temperature pressed off and obtained 3480 cc. juice, then added 105 grams more sugar to the juice and placed in 15° C. room until fermentation ceased.
- 1539—Same as 1538, except that yeast was propagated in fresh unsterilized pineapple must made to 18° Brix with cane sugar.
- 1540—1 part crushed pineapple and 2 parts 36° Brix cane-sugar solution, inoculated with new strain Tokay yeast propagated through 5 transplantings in sterilized grape must. After 24 hours at room temperature pressed off and to 5480 cc. juice added 200 grams cane sugar, jugged, and placed in 60° C. room until fermentation ceased.
- 1541—Same as 1540, except that yeast was propagated as in 1539.
- 1542—1 part crushed fresh pineapple and 1 part 45° Brix cane-sugar solution, inoculated with new strain Tokay yeast propagated through 5 transplantings in sterilized grape must. After 24 hours at room temperature pressed off, to 3260 cc. juice added 120 grams cane sugar, jugged, and placed in 15° C. room until fermentation ceased.
- 1543—Same as 1542, but inoculated as in 1539.

Analyses of the fermented solutions are given in the accompanying table.

Analyses of Fermented Solutions

No.	DATE INOCULATED (1925)	DATE ANALYZED (1925)	YEAST	FERMENTATION TEMP. ° C.	ALCOHOL VOL. %	ACIDITY (N alkali for 100 cc. soln.) Cc.	NITROGEN GEN. Grams per 100 cc.	SUGAR 100 cc.
241	8-10	9-23	Old Tokay	15	19.2	6.3		1.80
559	6-7	10-1	New Tokay	R ^a	12.8			
560	6-7	10-15	Old Tokay	R	14.1			
561	6-7	10-15	Mosel	R	13.5			
562	6-7	10-15	Steinberg	R	12.7			
602	6-14	9-15	Old Tokay	15	17.9	8.0	0.013	2.28
603	6-14	7-23	Old Tokay	R	15.6			
604	6-14	9-15	Old Tokay	15	17.6	7.5	0.013	2.30
605	6-14	9-15	New Tokay	15	19.2	8.5	0.010	0.74
606	6-14	7-22	New Tokay	R	16.8			
607	6-14	9-15	New Tokay	15	18.2	7.9	0.012	1.70
608	6-14	9-15	Steinberg	15	18.3	8.1	0.014	1.25
609	6-14	7-22	Steinberg	R	16.3			
610	6-14	9-15	Steinberg	15	15.6	10.5	0.016	4.39
611	6-14	9-15	New Tokay	15	18.3	8.8	0.013	0.13
612	6-14	7-22	New Tokay	R	17.2			
613	6-14	9-15	New Tokay	15	18.2	5.9	0.013	0.05
682	9-24	11-17	New Tokay	15	17.1			
683	9-24	11-12	New Tokay	R	17.1			
686	9-24	11-17	New Tokay	15	14.3			
687	9-24	11-13	New Tokay	15	18.3			
688	9-24	10-25	New Tokay	15	18.7			
1037	6-8	10-11	New Tokay	15	11.3			
1039	6-8	7-29	New Tokay	15	19.4			
1040	6-8	8-5	New Tokay	15	18.4			
1042	6-8	7-15	New Tokay	15	15.5			
1043	6-8	7-15	New Tokay	15	17.9			
1044	6-8	12-13	New Tokay	0-5	15.3			
1045	6-8	10-13	New Tokay	10	16.7	7.2		
1538	6-4	7-17	New Tokay	15	17.7			
1539	6-4	7-10	New Tokay	15	17.9			
1540	6-4	8-7	New Tokay	15	17.2			
1541	6-4	8-7	New Tokay	15	18.2			
1542	6-4	7-25	New Tokay	15	17.6			
1543	6-4	7-25	New Tokay	15	18.3			

^a R = room temperature.

Discussion

From the many experiments three factors that are essential to the formation of the high alcohol yields were discovered:

- (1) *Yeast Variety.* Of the different varieties of yeast used two wine yeasts predominate—Tokay and Steinberg. Of the two, the Tokay variety produces the higher alcohol concentrations. Compare 605 with 608; 606 with 609.
- (2) *Temperature of Fermentation.* The temperature at which

fermentation proceeds evidently cannot depart far from 15° C. if the maximum alcohol yield is to be obtained. Compare 605 with 606; 608 with 609; 1040 with 1045.

(3) *Fresh Fruit.* The must should consist, in part at least, of fresh fruit. In using sterilized or old concentrated fruit juices the alcohol formation never attained the high points yielded with fresh fruits. Compare 241 with 559-60-61-62; also 1040 with 1037. It is strange that sugared pineapple must, without much water addition, shows less attenuation than a must composed of 1 part pineapple and 2 parts 35 per cent sugar solution. Compare 1040 with 1042. With grape must the opposite is true. Compare 682 with 687 and 688.

There is little need for discussion in regard to the yeast strains and the temperature controls of these fermentations, as it is well known that different yeasts possess different fermentative powers, which are in turn greatly influenced by the temperature. On the other hand, the striking differences in behavior of the same yeast in a must composed wholly or in part of fresh fruit, and in the same must after pasteurization or sterilization, seem to offer a fertile field for further work and speculation. Does the fresh fruit contain some vitamin,

hormone, or bios, which is destroyed or precipitated by heat or age, that stimulates the yeast to extra endeavor or makes it immune to alcoholic concentrations that otherwise would inhibit its functions? Or do these fresh fruits have a favorable balance of food constituents that is disturbed by precipitation or alteration when heated or aged? The writers are unable to answer these questions now, but the investigations will be continued with the object of clearing up the matter. The fact that the addition of small amounts of urea (compare 1039 with 1040; 1042 with 1043) to the must increases the production of alcohol suggests that the nature of the nitrogenous constituents may be one explanation. Without doubt the manner of propagating the yeast also has a decided effect (compare 1540 with 1541; 1542 with 1543). There is reason to believe that yeast revived from agar transplants is more potent than yeast that has been kept in liquid media for long periods. Whatever it is that occurs in fresh fruit to make it the splendid medium it is, the pineapple is unusually favored with it.

Mechanism of the Baking Process of Oil Varnishes¹

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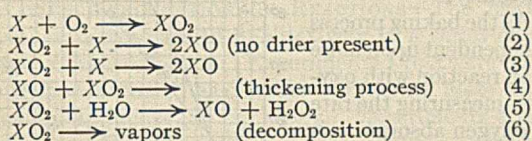
BEFORE any object which has been given a coat of varnish or enamel is ready for use, the varnish film must be converted to the solid state. This is accomplished either by allowing the film to air-dry or by baking. In spite of the extensive industrial use of baking, very little is known of what actually takes place and practically nothing of the fundamental laws that govern the process.

An attempt is made to gain insight into the mechanism of the baking process of oil varnishes. To measure the degree of baking, a colorimetric method was developed. Using this method of evaluation, data are presented for the baking process of a typical oil varnish in air, oxygen, nitrogen, hydrogen, and vacuum. It is shown that the process can be written in the form of a chemical equation which, in its general form, is composed of two factors—one involving oxidation, the other polymerization. When only the latter occurs, the baking process is shown to be independent of the nature of the gas. Furthermore, it was found that the logarithm of the time to attain any decided degree of baking varies linearly with the reciprocal of the absolute temperature.

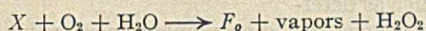
As to the baking process itself, very few investigations have been reported, although Leeds (3), Long, Knauss, and Smull (4), Morrell (5), Nagel and Gruss (7), Rhodes and Welz (8), Salway (9), Schumann (10), and Wolff (11) studied in some detail the reactions that occur in the thermal treatment of drying oils prior to and during the manufacture of varnishes. They show that heat causes a tying up of the oil molecules—that is, polymeriza-

Historical

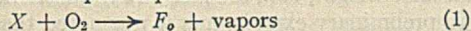
Various investigators have studied the setting process of oil varnishes at ordinary temperatures, and their results indicate that several types of reactions occur. Morrell (6) summarized these investigations, writing the reactions schematically as follows:



where X represents the oil molecule. Combining the above reactions and letting F_o represent the varnish or oil film produced, we obtain for the setting process in ordinary air, the equation



or, for dry air, the simpler expression



an equation to which reference is made later.

They point out that the polymerization reactions are quite distinct from those which take place with oxygen, and that under certain conditions both occur simultaneously. They give, as the changes that occur on heating, increase in viscosity, increase in density, decrease in hexabromide number, increase in acid value, decrease in iodine value, and increase in apparent molecular weight. They show that polymerization is independent of the atmosphere in which it is carried out. As baking fundamentally involves heat, polymerization must be considered in the setting process of a varnish where baking is employed.

Theoretical

When an oil varnish is exposed in a thin film to any given set of conditions, primarily two things can occur—namely, (a) evaporation of the solvents; and (b) conversion of the base to a *useful* state which we refer to, practically, as the dry or baked state.

EVAPORATION OF THE SOLVENTS—The evaporation of the solvents is a simple process and is expressed algebraically by the equation



where V refers to any oil varnish or enamel, B represents the varnish base, and ΣS the solvent or solvents.

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