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A STUDY OF THE SOFT RESINS IN SULPHURED AND UNSULPHURED HOPS IN COLD AND IN OPEN STORAGE.

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INTRODUCTION.

During the past decade the soft resins of hops have been the subject of numerous investigations which have dealt almost exclusively with the percentage of yield and the methods of extraction. With the exception of the work of Fischer,¹ no statements have been found in the literature to show that recognized chemical methods have been used to determine the changes which occur in the soft resins of hops subsequent to harvesting. The effect of refrigeration on the physical condition and on certain chemical constituents of sulphured and unsulphured hops has been studied by Stockberger and Rabak,² who gave special consideration to the changes which occur in the volatile oil. Aside from the changes noted by these authors, extensive modifications also occur in the soft resins of hops, the character of which may be determined through the use of reliable analytical methods.

¹ Fischer, Alfred. Analysis of hops as a basis for their valuation. *In* Pure Products, v. 8, no. 10, p. 536-538. 1912.

² Stockberger, W. W., and Rabak, Frank. Some effects of refrigeration on sulphured and unsulphured hops. U. S. Dept. Agr., Bur. Plant Indus. Bul. 271, 21 p. 1912.

NOTE.—This bulletin presents the results obtained from experiments conducted to determine the extent and character of the changes in the soft resins in hops under varying conditions of curing and storage. The soft resins, or so-called bitter acids, are a principal factor in determining the commercial value of hops.

In order to obtain additional data regarding the effect of various storage conditions upon the soft resins of sulphured and unsulphured hops, a quantity of material was prepared and held under observation for several years. The data secured indicate that there is a marked chemical rearrangement or balancing of at least a part of the components of these resins during the first year after the hops are harvested. This rearrangement is most marked in hops kept in cold storage, and of these it is most evident in the unsulphured hops.

It is generally conceded that the commercial value of hops is almost entirely contingent upon two considerations, namely, the character of the aroma and the nature and quantity of the soft resins. At the last International Hop and Barley Exhibit, held in Chicago in 1911, the score card gave an equal rating to aroma and to the soft resins, or, as they are sometimes termed, the hop bitter acids.

Although sulphuring and cold storage are efficient factors in retarding the diminution of the quantity of soft resins in hops, they do not prevent chemical changes from taking place therein. Nevertheless, the data obtained by the study of these changes indicate that they are influenced to a considerable degree by both sulphuring and cold storage. The experiments detailed in the following pages were made with a view to determining the extent and character of these changes.

PREPARATION OF THE HOPS STUDIED.

Since soil and climate, as well as other factors, are undoubtedly responsible for the varying quantity of soft resins found in hops of different geographical origin, all the samples of hops used in this investigation were secured from a common source, in order to eliminate variation so far as possible. Accordingly, two lots of hops harvested from the same field at Perkins, Cal., in September, 1911, were dried in ordinary hop kilns, one portion without being sulphured, the other receiving the customary sulphuring in the early stages of drying. Duplicate samples of each lot were then placed in hermetically sealed tin cans and shipped to Washington, D. C. About the 1st of December one sample each of the sulphured and unsulphured hops was subjected to analysis, and the remaining samples, each weighing 2 kilograms, were then removed from the tins, compressed to about the same degree as the hops in a commercial bale, and completely inclosed in a cover of ordinary hop sacking. Three each of these sulphured and unsulphured samples were then placed in cold storage in the hop storeroom of a local brewery, and a similar set of samples was placed in the attic of a frame building at the Arlington Experiment Farm, Virginia. On December 1 of each of the three following years one sample each of the sulphured and the unsulphured hops was withdrawn from cold and open storage, respectively, and subjected to analysis.

CHANGES IN PHYSICAL APPEARANCE.

On receipt of the various samples of hops from Perkins, Cal., in 1911, they were examined and the following notes taken respecting their physical characteristics:

Sulphured hops in the original lot.—Fine fresh hop flavor; oily feeling; lupulin sticky; aroma excellent; color bright, characteristic of new fresh hops; color of lupulin bright.

Unsulphured hops in the original lot.—Fine fresh hop flavor; oily feeling; lupulin sticky; aroma excellent; color bright, characteristic of new fresh hops, though somewhat greener in appearance than the corresponding sulphured sample; color of lupulin bright.

On December 1 of the three following years, two samples each from cold and from open storage were examined and the following notes were taken on their physical characteristics:

Sulphured hops in cold storage one year.—Fresh hop flavor; oily feeling; lupulin sticky; aroma good; color darker than the original sample, not so bright and characteristic; color of lupulin bright.

Unsulphured hops in cold storage one year.—Fresh hop flavor; oily feeling; lupulin sticky; aroma good; color much darker than the original sample, not so bright and characteristic; color of lupulin bright.

Sulphured hops in open storage one year.—Strawlike flavor; oily feeling; lupulin less sticky; aroma disagreeable; color dull, bright color having disappeared; color of lupulin dull.

Unsulphured hops in open storage one year.—Strawlike flavor; oily feeling less noticeable; lupulin less sticky; aroma disagreeable; color very dull; color of lupulin dull.

Sulphured hops in cold storage two years.—Decided strawlike flavor; oily feeling very slight; lupulin slightly sticky; aroma slightly hoplike; color dark yellow, brightness having disappeared; color of lupulin dull.

Unsulphured hops in cold storage two years.—Most decided strawlike odor, somewhat musty; oily feeling practically gone; lupulin not sticky; aroma like musty straw; color dark brownish yellow; color of lupulin very dull.

Sulphured hops in open storage two years.—Decided strawlike flavor; oily feeling practically gone; lupulin slightly sticky; aroma that of musty straw; color dark brownish yellow; color of lupulin very dull.

Unsulphured hops in open storage two years.—Very decided musty flavor; oily feeling gone; lupulin very slightly sticky; aroma that of musty straw; color dark brownish yellow; color of lupulin very dark and dull.

Sulphured hops in cold storage three years.—Most decided strawlike flavor, somewhat musty; oily feeling gone; lupulin very slightly sticky; aroma that of old musty straw; color dark brownish yellow; color of lupulin very dark and dull; hop cones falling apart.

Unsulphured hops in cold storage three years.—Very decided musty, strawlike flavor; oily feeling entirely gone; lupulin not sticky; aroma that of old musty straw; color very dark, dirty brownish yellow; color of lupulin very dark and dull; hop cones falling apart.

Sulphured hops in open storage three years.—Very decided musty, strawlike flavor; oily feeling entirely gone; lupulin not sticky; aroma that of old musty straw; color dark brownish yellow; color of lupulin very dark and dull; hop cones fallen apart.

Unsulphured hops in open storage three years.—Most decided musty, strawlike flavor; oily feeling entirely gone; lupulin not sticky; aroma that of old musty straw; color very dark brownish yellow; color of lupulin very dark and dull; hop cones fallen apart.

As far as physical valuation indicates, the sulphured hops in cold storage deteriorated at a slower rate than the unsulphured hops, and the same is true for the samples placed in open storage. At the end of one year of storage very little physical difference could be noticed in the cold-storage hops other than that the color had darkened in both the sulphured and unsulphured samples, more especially in the latter. The samples in open storage at the end of one year had each developed a strawlike odor and had become dull in color. The lupulin of both the sulphured and unsulphured hops had begun to lose its brightness and its sticky feeling.

At the end of the second year of storage a most decided change had taken place in all the samples. The sulphured hops in cold storage had developed a strawlike flavor and a dry feeling and the bright color had disappeared. The unsulphured samples had developed a musty odor and an extremely dry feeling, and the characteristic greenish yellow color had disappeared. The unsulphured hops had deteriorated more rapidly than the corresponding sulphured hops. So far as the physical valuation indicated, the hops in open storage had deteriorated to a much greater degree than the hops in cold storage. The unsulphured samples in open storage had become very musty in odor and very dark in color, in addition to losing their crisp and sticky feeling.

At the close of three years of storage the samples had lost all traces of hop flavor and had developed a musty, strawlike odor. A slight stickiness could still be detected in the sulphured hops in cold storage. The hop cones in the cold-storage samples had fallen apart to some extent, whereas those in the open storage samples had completely fallen apart. The lupulin in all the samples was much discolored.

MOISTURE CONTENT AND CHANGES IN THE PROPORTION OF SOFT AND HARD RESINS.

At the time the hops were received in Washington a sample each of the sulphured and unsulphured hops was analyzed and the results thus obtained were used as the basis for comparing the analyses which were made of the various samples during each year of storage.

MOISTURE CONTENT.

For the determination of the moisture content 12 grams of hops were taken from each of the samples under investigation, dried over sulphuric acid until of constant weight, and the loss in weight returned as moisture. The moisture content of the original hops and of the hops in both cold and open storage for the several years is given in Table I.

TABLE I.—*Moisture in the original samples of sulphured and unsulphured hops and in samples kept in cold and in open storage.*

Treatment at the kiln.	Original sample, 1911.	Cold storage.			Open storage.		
		1912	1913	1914	1912	1913	1914
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
Sulphured.....	6.18	11.04	11.04	9.83	5.81	6.37	6.40
Unsulphured.....	5.23	10.90	10.79	10.90	6.14	5.90	5.50

From Table I it is evident that the moisture content of the hops kept in cold storage was greater than of those in open storage. In the samples kept in cold storage the moisture content was very uniform for the three years in both the sulphured and the unsulphured hops, indicating that the cold-storage room was kept at a uniform temperature throughout this period. In the open-storage samples a slight fluctuation in the moisture content was evident, due apparently to differences in the atmospheric conditions at the time the samples were removed for analysis. Since moisture is an important adjunct to a great many chemical changes, it is probable that the greater quantity found in the samples kept in cold storage had a direct bearing on the chemical changes that took place in the soft resins.

SOFT RESINS.

In determining the quantity of soft resins in the hop samples, a departure was made from the method usually employed. A kilogram of hops was extracted by maceration and percolation with petroleum ether (B. P. 35° C. to 70° C.). Two macerations were necessary to complete the extraction. The mixed percolates were then heated on a water bath at 70° C. and the major portion of the petroleum ether recovered. The remainder of the petroleum ether was allowed to evaporate spontaneously and the weight of the residue returned as soft resins. The residues each contained a small fraction of approximately 0.4 per cent of wax, which for purposes of comparison may be disregarded. The percentage of soft resins in the original sulphured and unsulphured samples and in the corresponding samples in cold and in open storage is shown in Table II.

TABLE II.—*Soft resins in the original samples of sulphured and unsulphured hops and in samples kept in cold and in open storage.*

Treatment at the kiln.	Original sample, 1911.	Cold storage.			Open storage.		
		1912	1913	1914	1912	1913	1914
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
Sulphured.....	12.32	11.91	11.46	4.98	11.32	9.03	3.20
Unsulphured.....	11.17	9.72	8.66	3.81	8.73	7.43	2.32

Regarding, first, the sulphured hops, the data in Table II show that the percentage of soft resins decreased somewhat during the first and second years of storage and very rapidly during the third year. The decrease was less, however, in the cold-storage samples than in those kept in open storage. The unsulphured hops show a marked decrease from year to year, the decrease being most pronounced in the third year of storage. The unsulphured samples in open storage show a greater loss than the corresponding samples

kept in cold storage. During the first year of open storage the soft-resin content in the sulphured hops decreased less rapidly than in the unsulphured hops, but more rapidly in the following two years.

It will be observed from figure 1 that the quantity of soft resins present in the sulphured hops in both cold and open storage decreased during each year and that the decrease was especially marked during the third year of storage. Figure 1

FIG. 1.—Curves of the percentage of soft resins in sulphured and unsulphured hops in cold and in open storage.

also shows that the unsulphured hops in cold storage decreased in soft-resin content more rapidly than the sulphured hops and that this decrease was rapid during the first year, less pronounced during the second year, and at the end of the third year gradually approached the same point of value as in the sulphured hops in cold storage. The soft-resin content of the unsulphured hops in open storage decreased at about the same rate as that of the sulphured hops in open storage.

The percentage of decrease in soft resins during the three years, as compared with the original samples, is given in Table III.

TABLE III.—*Decrease in the soft resins of sulphured and unsulphured hops in cold and in open storage compared with the soft-resin content of the original samples.*

Treatment at the kiln.	Original sample, 1911.	Cold storage.			Open storage.		
		1912	1913	1914	1912	1913	1914
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
Sulphured.....	100	3.32	6.98	59.57	8.11	26.71	74.02
Unsulphured.....	100	12.98	22.47	65.89	21.84	33.48	79.23

From Table III, in which the soft-resin content in the original samples is considered as 100 per cent, it is evident that the decrease in the sulphured hops during the first two years in cold storage was not great, but it was rapid during the third year. In open storage the decrease was very pronounced during each year. The unsulphured hops in cold storage show a marked decrease, which was greatest in the third year, and in open storage the decrease was even more pronounced year by year.

HARD RESINS.

The hard resins in the various samples of hops used in this study were also determined. A portion of the hops after being extracted with petroleum ether was again extracted with ether, the ether recovered, and the weight of the residue returned as hard resin. By this method an extra calculation is necessary, but in using large quantities of hops the time consumed is more than compensated for in the accuracy obtained.

The hard-resin content of the various samples is shown in Table IV.

TABLE IV.—*Hard resins in the original samples of sulphured and unsulphured hops and in samples kept in cold and in open storage.*

Treatment at the kiln.	Original sample, 1911.	Cold storage.			Open storage.		
		1912	1913	1914	1912	1913	1914
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
Sulphured.....	5.26	6.53	8.97	9.90	8.32	9.09	10.10
Unsulphured.....	6.43	8.35	10.08	10.05	9.53	10.45	10.46

The figures in Table IV give an index of the change in the quantity of hard resins that took place in the various hop samples. The greatest change occurred in the unsulphured hops in open storage and the least change in the unsulphured hops during the first two years in cold storage. The difference in the content of hard resins of both sulphured and unsulphured hops in cold and in open storage, respectively, became materially less in the third year of storage and probably indicates that the changes which took place in the hops

tended to reach a state of equilibrium irrespective of the treatment of the sample.

Figure 2 gives a graphic representation of the increase in the hard-resin content of sulphured and unsulphured hops in cold and in open storage.

During the first year the increase in the hard-resin content in the sulphured hops was greater in open storage than in cold storage. At the end of the second year the sulphured hops in both cold and

FIG. 2.—Curves of the percentage of hard resins in sulphured and unsulphured hops in cold and in open storage.

open storage contained about the same percentage of hard resins. The unsulphured hops followed the same lines, but did not present quite so marked a difference during the first year of storage. At the end of the third year the hard-resin content in all the samples had become uniform and a state was reached where the increase, if any, was very slow.

Table V gives the percentage of increase in the hard-resin content of the various samples as compared with the original, the hard-resin content of the latter being considered as 100 per cent.

TABLE V.—Increase in the hard resins of sulphured and unsulphured hops in cold and in open storage, compared with the hard-resin content of the original samples.

Treatment at the kiln.	Original sample, 1911.	Cold storage.			Open storage.		
		1912	1913	1914	1912	1913	1914
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
Sulphured.....	100	24.14	70.53	88.21	58.17	72.81	92.01
Unsulphured.....	100	29.85	52.75	56.29	48.21	62.51	62.67

The sulphured hops appeared to react less readily to changes that bring about an increase in the hard resins. From this it is inferred that sulphuring is a factor that retards the changing of soft resins to hard resins. This is shown most emphatically in Table V by the fact that the percentage of increase in the unsulphured hops was much less in both cold and open storage than in the corresponding sulphured

hops. A further study of Table V indicates that a combination of sulphuring and cold storage was most effective in retarding the changes that produce hard resins.

TOTAL RESINS.

The total resin content of the various hop samples, found by adding the soft resins and the hard resins together, is shown in Table VI.

TABLE VI.—*Total resins in the original samples of sulphured and unsulphured hops and in samples kept in cold and in open storage.*

Treatment at the kiln.	Original sample, 1911.	Cold storage.			Open storage.		
		1912	1913	1914	1912	1913	1914
Sulphured.....	<i>Per cent.</i> 17.58	<i>Per cent.</i> 18.44	<i>Per cent.</i> 20.43	<i>Per cent.</i> 14.88	<i>Per cent.</i> 19.64	<i>Per cent.</i> 18.12	<i>Per cent.</i> 13.30
Unsulphured.....	17.60	18.07	18.74	13.86	18.26	17.88	12.78

From the figures in Table VI it appears that some discrepancies exist, since the total resins in some years ran higher than those of the original sample. Experiments in this laboratory have shown that two samples are rarely ever the same in total yield of resins; hence, no weight need be attached to the apparent discrepancies.

The sudden decrease in the total resins in all the samples in the year 1914 is of special interest. Up to this point the hops in storage had retained approximately their original content of soft resins. A marked diminution now occurred in the content of soft resins, which is not compensated by a corresponding increase in the content of hard resins. It appears from the data at hand that a portion of the soft resins had been transformed into a compound or compounds insoluble in ether or in petroleum ether, since the marked loss in percentage of soft resins does not appear in the ether extract. The extent of the change was greatest in the unsulphured hops in open storage and least in the sulphured hops in cold storage, but in all samples, irrespective of treatment either at the kiln or during storage, the decrease was rapid. Table IV shows that at the end of the second year of storage a point was reached by all the samples beyond which the hard resins did not materially increase. Nevertheless, at this point the soft resins began to decrease most rapidly. Although previous investigators have stated that the soft resins change entirely to hard resins, it is probable that only a small portion of the soft resins undergoes such a change, and the remainder is changed into a compound or compounds insoluble in the solvents used in extraction and for that reason is lost sight of in the analysis.

TABLE VII.—*Soft resins in the original samples of sulphured and unsulphured hops and in samples kept in cold and in open storage, calculated with reference to the total resins.*

Treatment at the kiln.	Original sample, 1911.	Cold storage.			Open storage.		
		1912	1913	1914	1912	1913	1914
Sulphured.....	<i>Per cent.</i> 70.13	<i>Per cent.</i> 64.59	<i>Per cent.</i> 56.08	<i>Per cent.</i> 33.47	<i>Per cent.</i> 57.63	<i>Per cent.</i> 49.83	<i>Per cent.</i> 24.06
Unsulphured.....	63.46	53.79	46.21	27.49	47.80	41.55	18.15

The data in Table VII show that the sulphured cold-storage hops retained a greater percentage of soft resins each year than did any of the other samples. The unsulphured hops in cold storage and the sulphured hops in open storage contained year by year practically the same percentage of soft resins, as calculated with reference to the total resins. The greatest decrease is noted in the soft resins from the unsulphured hops in open storage.

CHANGES IN THE COMPOSITION OF THE SOFT RESINS.

That chemical changes take place in the soft resins of hops is a foregone conclusion. In order to study these changes, methods in general use in chemistry, with some modifications, were applied to the soft resins with satisfactory results. The physical properties of color and odor presented in Table VIII were observed from year to year.

TABLE VIII.—*Physical properties of the soft resins in the original samples of sulphured and unsulphured hops and in samples kept in cold and in open storage.*

Treatment at the kiln.	Original sample, 1911.	Cold storage.		
		1912	1913	1914
Color:				
Sulphured.....	Greenish brown.	Dark brown....	Greenish brown.	Greenish black.
Unsulphured.....	Dark brown....	Very dark brown.	do.....	Do.
Odor:				
Sulphured.....	Aromatic, pleasant.	Aromatic, pleasant.	Aromatic, pleasant.	Aromatic, un-
Unsulphured.....	do.....	Aromatic, pungent.	Agreeable, hop-like.	pleasant. Do.
Treatment at the kiln.	Original sample, 1911.	Open storage.		
		1912	1913	1914
Color:				
Sulphured.....	Greenish brown.	Dark brown....	Greenish brown.	Greenish black.
Unsulphured.....	Dark brown....	do.....	do.....	Do.
Odor:				
Sulphured.....	Aromatic, pleasant.	Aromatic, pleasant.	Aromatic, pleasant.	Disagreeable, somewhat aromatic.
Unsulphured.....	do.....	Aromatic, pungent.	Aromatic, pungent.	Do.

All the samples had an extremely bitter taste, manifested strongly at the base of the tongue when a minute particle of the soft resin was held in the mouth for a few seconds.

The color, odor, and taste, which appeal solely to the senses, are of relatively small importance in this investigation. As shown in Table VIII, the color of the soft resins in all cases became darker with the age of the sample examined; the odor became very disagreeable with the decrease of the soft resins and the taste at all times remained very bitter.

The soft resins are fluid in nature, and during the first two years of storage all were of the same consistency. Those extracted in 1914 were more solid and had the consistency of a thick sirup. Owing to their nature, the specific gravity of these resins could not be determined with accuracy.

ACID AND ESTER VALUES.

The determination of the free acidity or acid value of the soft resins was carried out as follows: A small quantity of weighed soft resin was taken up in 2 c. c. of standardized alcoholic potassium hydroxid and the excess potassium hydroxid titrated back with N/10 hydrochloric acid. The acid value represents the number of milligrams of potassium hydroxid necessary to completely neutralize the free acids in 1 gram of the soft resins.

In determining the ester value of the soft resins a weighed portion was taken up in standardized alcoholic potassium hydroxid and allowed to stand 24 hours in the cold. Complete saponification took place in that length of time. The excess alkali was titrated back with N/10 hydrochloric acid and the saponification value calculated. This value, minus the acid value, gives the ester value of the soft resins and represents the number of milligrams of potassium hydroxid necessary to completely saponify all the combined acids in 1 gram of the soft resins. The changes observed in the acid and ester values are shown in Table IX.

TABLE IX.—*Acid and ester values of the soft resins in the original samples of sulphured and unsulphured hops and in samples kept in cold and in open storage.*

Treatment at the kiln.	Original sample, 1911.	Cold storage.			Open storage.		
		1912	1913	1914	1912	1913	1914
Acid value:							
Sulphured.....	71.80	97.00	87.50	80.7	72.5	61.50	47.0
Unsulphured.....	60.87	67.00	76.50	76.2	52.0	70.00	77.6
Ester value:							
Sulphured.....	97.7	169.5	191.1	226.3	122.5	202.5	271.0
Unsulphured.....	121.78	71.5	87.0	207.8	123.5	158.0	158.4

A graphic representation of the acid values is given in figure 3. From this figure it will be seen that after the first year of storage the acid value of the soft resins diminished in the sulphured hops and gradually increased in the unsulphured hops. The rise in acid value of the soft resins of the sulphured hops during the first year in cold storage was probably due to the rearrangement that was taking place in these resins; although esters were formed during this period the esterification did not proceed as rapidly as in the following years, with a consequent rise in free-acid value. During the first year of open storage the acid value of the soft resins of the sulphured hops remained about the same and then gradually decreased at a rate proportionate to that of the sulphured hops in cold storage. The formation of esters was slow during the first year of storage and rapid

during the next two years, reaching a slightly higher value at the end of the third year than in the corresponding sample in cold storage.

The unsulphured hops in cold storage yielded soft resins whose acid value constantly increased throughout the period of storage. The ester value for these soft resins decreased

FIG. 3.—Acid-value curves of the soft resins in sulphured and unsulphured hops in cold and in open storage.

during the first year, then gradually increased during the second year, and very rapidly during the third year of storage. In open storage the acid value in the unsulphured hops was slightly less at the end of the first year than in the corresponding original sample. The ester value (fig. 4) remained almost constant, indicating that there was little change in these values during the first year of storage. From this point the acid values from the unsulphured hops increased gradually, until at the end of the third year of storage about the same degree of acidity was reached.

The increase in acidity was, however, most marked in the unsulphured hops in open storage. The ester values for the soft resins of the unsulphured hops increased after the first year of storage and was most rapid in the cold-storage samples.

The acid value of the soft resins from sulphured hops in both cold and open storage gradually diminished at approximately the same rate after one year of storage. The corresponding ester values in-

creased in approximately the same proportion as the acid values diminished. This decrease in the acid value and increase in ester value would indicate that esterification took place faster than free acids were formed, the original quantity of free acids being practically used up. In other words, the sulphuring of hops appears to hasten the formation of esters in the soft resins but retards the formation of free acids.

The acid value of the soft resins from the sulphured hops in both cold and open storage gradually increased during the period of storage, and the corresponding ester value

FIG. 4.—Ester-value curves of the soft resins in sulphured and unsulphured hops in cold and in open storage.

FIG. 5.—Saponification-value curves of the soft resins in sulphured and unsulphured hops in cold and in open storage.

likewise gradually increased, indicating that in the unsulphured hops the formation of free acids and of the corresponding esters goes on with regularity.

SAPONIFICATION VALUE.

The saponification value, shown in Table X and indicated graphically in figure 5, was in this study determined before the ester value, although it is usually obtained by adding

the acid and ester values of the product under investigation. From

a study of the ester and acid values, a gradual increase in the saponification value would be expected. This increase was most marked after the first year of storage, and all the samples gradually approached a uniform value. The saponification value of the soft resins from the sulphured hops was slightly higher than the same value in the unsulphured hops. The increase in the saponification value was most uniform in the hops held in open storage and was most rapid during the third year in the unsulphured hops in cold storage.

TABLE X.—*Saponification value of the soft resins in the original samples of sulphured and unsulphured hops and in samples kept in cold and in open storage.*

Treatment at the kiln.	Original sample, 1911.	Cold storage.			Open storage.		
		1912	1913	1914	1912	1913	1914
Sulphured.....	169.5	266.5	278.5	317	195	264	324
Unsulphured.....	182.65	138.5	163.5	284	175.5	228.5	236

IODIN VALUE.

In determining the iodine-absorption value of the soft resins, the method employed was that commonly used in determining this value in fats. The results obtained are shown in Table XI.

TABLE XI.—*Iodine value of the soft resins in the original samples of sulphured and unsulphured hops and in samples kept in cold and in open storage.*

Treatment at the kiln.	Original sample, 1911.	Cold storage.			Open storage.		
		1912	1913	1914	1912	1913	1914
Sulphured.....	95	76	144	156	123	132	156
Unsulphured.....	100	72	140	141	89	143	153

The iodine values, as shown in Table XI and in figure 6, became less divergent in the third year of storage. In the soft resins from the sulphured hops in open storage the iodine value gradually increased for each year of storage. In all the other samples it diminished during the first year, rose rapidly during the second year, and in the third year was uniform with that from the sulphured hops in open storage. This indicates a diminution in the unsaturated compounds in the soft resins from the sulphured hops in cold storage and from the unsulphured hops in both cold and open storage and an increase in the unsaturated compounds in sulphured hops in open storage during the first year. It will be noted, however, that after the completion of the marked readjustment that took place during the first year of storage, the iodine value of all the samples tended to become uniform, thus indicating that the unsaturated compounds were present in approximately the same proportion in all the soft resins of all the hop samples at some point between the first and the second year of storage.

CHEMICAL VALUES OF THE SOFT RESINS.

In order to make more apparent the correlation between the various chemical values found in the soft resins from year to year, these values have been brought together and are represented graphically in figures 7, 8, 9, and 10.

Figure 7 shows the various values as found in the sulphured hops in cold storage. The acid value, which increased during the first year of storage, gradually decreased during the second and third years.

The ester value, which increased very rapidly during the first year of storage, diminished somewhat during the next two years. Figure 7 shows also that although esterification took place rapidly during the first year of storage it could not keep

pace with the formation of free acids; thus the latter increased. During the remainder of the time the hops were in storage esterification continued, but the quantity of free acids formed was not so great, with the result that there was a decrease in free acidity.

The saponification value gradually increased throughout the storage period.

The iodine value at

FIG. 7.—Curves showing the correlation of chemical values of the soft resins in sulphured hops in cold storage.

the end of the first year of storage was less than that of the original sample, indicating that the formation of unsaturated compounds in the soft resins had been retarded in the sample held in storage. The iodine value increased during the second year, indicating a greater production of unsaturated compounds in the soft resins.

FIG. 6.—Iodin-value curves of the soft resins in sulphured and unsulphured hops in cold and in open storage.

Figure 8 shows the various values as found in the sulphured hops in open storage. The acid value, which remained almost constant

during the first year of storage, gradually diminished during the next two years. The ester value, which increased somewhat during the first year, increased rapidly during the second and third years, indicating that the esterification was slightly in advance of the formation of free acids at all periods of storage and became more pronounced at the close of the third year. The iodine

FIG. 8.—Curves showing the correlation of chemical values of the soft resins in sulphured hops in open storage.

value gradually increased, indicating the continuous formation of unsaturated compounds in the soft resins throughout the entire period of storage. The saponification value gradually increased throughout the period of storage.

Figure 9 gives a graphic illustration of the various values as found in the unsulphured hops in cold storage. The acid value gradually increased throughout the period of storage. The ester value diminished during the first year of storage, increased somewhat during the second year, and in the third year the increase was rapid. Figure 9 shows also that esterification did not keep pace with the formation of free acids during the first year of storage. However, during the next

FIG. 9.—Curves showing the correlation of chemical values of the soft resins in unsulphured hops in cold storage.

Figure 9 shows also that esterification did not keep pace with the formation of free acids during the first year of storage. However, during the next

two years it was more rapid, with a consequent increase in the ester value.

The saponification value gradually increased after the first year of storage. The iodine value likewise increased after the first year, although during that year it diminished somewhat, but during the second year it increased rapidly, indicating thereby that the unsaturated compounds formed in the soft resins also increased rapidly, and they remained fairly constant after this point was reached until the close of the third year.

Figure 10 shows the various values as found in the unsulphured hops in open storage. The acid value diminished slightly during the first year and increased each year thereafter. The ester value increased slightly during the first year, quite rapidly during the second year, and remained constant during the third year, esterification in this sample practically keeping pace with the formation of free acids throughout the storage period. The saponification value, which decreased slightly

FIG. 10.—Curves showing the correlation of chemical values of the soft resins in unsulphured hops in open storage.

during the first year of storage, increased during the second and third years. The iodine value decreased slightly during the first year, increased rapidly during the second year, and slightly during the third year, indicating thereby that the unsaturated compounds in the soft resins remained fairly constant during the first year, increased rapidly during the second year, and were fairly constant during the third year of storage.

The relations of these various values may be briefly summarized as follows:

(1) A change took place in some of the components of the soft resins of the hops, indicative of a marked rearrangement in these compounds during the period that elapsed between picking the hops and the end of one year of storage.

(2) This change was most pronounced in the hops in cold storage, irrespective of treatment at the dry kiln. However, on comparison, the unsulphured hops showed the greatest change.

(3) This change was not so pronounced in the hops kept in open storage, irrespective of treatment at the dry kiln. On comparison, however, the unsulphured hops showed the greatest change.

(4) The most decided change occurred in the unsulphured hops in cold storage and the least marked change in the sulphured hops in open storage.

(5) After the first year the degree of change in all the samples fluctuated with regularity from year to year. Taken in the aggregate, the values as determined from year to year indicate most strongly that an extensive rearrangement took place in the soft resins of the hops from the time they were picked until some point was reached between the first and second year of storage. When this point was reached and the rearrangement had practically terminated, a gradual increase or decrease could be traced in all the values taken.

SUMMARY.

In 1911, material for a comparative study of the soft resins of sulphured and unsulphured hops in both cold and open storage was secured from a hop ranch at Perkins, Cal. The green hops were divided into two lots, one of which was sulphured during the process of drying. The dry sulphured and unsulphured hops were again divided into lots, sealed in tin cans, and shipped to Washington, D. C. On arrival the cans were opened and an analysis made of one lot each of the sulphured and unsulphured hops. The remaining samples were baled in burlap and three samples each of the sulphured and unsulphured hops were placed in both cold and open storage.

At the end of the first, second, and third years of storage one sample each of the sulphured and unsulphured hops was withdrawn from both cold and open storage and an analysis made of each. The hops analyzed in 1911 are designated as "original hops," since they approximate more nearly the condition of the samples at the time of drying.

A physical valuation was placed on the original samples and also on the hops as they were withdrawn from storage from time to time. From these valuations the conclusions are drawn that both sulphuring and cold storage retard changes in the physical characteristics of hops. A combination of the two factors is more effective in retarding these changes than either factor alone.

Determinations were made of the moisture, the percentage of soft resins, hard resins, and total resins, of the color, odor, and taste of the soft resins, and of the acid, ester, saponification, and iodine values of the soft resins.

The moisture content in the sulphured and unsulphured hops held in cold storage increased during the first year and then remained practically constant in all the samples throughout the period of storage. The moisture content of the sulphured and unsulphured hops in open storage varied from year to year, according to existing weather conditions.

The percentage of soft resins in all the samples decreased with each year of storage, becoming very pronounced in the third year. The percentage of hard resins in all the samples increased with each year of storage, approaching a uniform figure at the close of the third year. Both sulphuring and cold storage retarded the decrease in the percentage of soft resins and increased the percentage of hard resins. A combination of the two factors was more effective in retarding these changes than either factor alone.

The percentage of total resins in all the samples varied from year to year, and in the third year it became materially less than that of the original sample. The low total is probably due to the formation of products insoluble in the solvents used.

The color, odor, and taste of the soft resins are of very little value in determining quality and are not indicative of any changes that may have taken place therein.

The acid value in general decreased in the sulphured hops in cold and in open storage and increased in the unsulphured hops in cold and in open storage. Sulphuring apparently retards the formation of free acids, and a combination of sulphuring and cold storage is most effective in retarding changes in free acidity.

The ester value in general increased in all the samples of hops. Sulphuring apparently favors the formation of esters, and this factor in combination with open storage appears to be the least effective in retarding the formation of esters. Nonsulphuring and open storage appear to be the most effective in retarding the formation of esters.

The saponification value in general increased in all the samples of hops. The unsulphured hops showed the least change, and of these the ones held in open storage were the least affected.

The iodine value in general increased in all the samples. It was most pronounced in the second year of storage and in the third year was uniform in all the samples. Sulphuring in combination with open storage appears to cause a uniform rate of increase in the iodine value from year to year. The sulphured hops in open storage showed the least variation in changes in the chemical values of the soft resins.

During the period of storage, at least some of the components of the soft resins underwent rearrangement. This rearrangement was most marked during the first year, after which it decreased to such an extent that thereafter comparable values for the chemical constants were readily obtained.