It may be seen that this lime contains very little iron oxide. It is evident therefore that we must look elsewhere for the sources of the iron which caused the trouble in the pan.

Some iron doubtless came from the lime, and some unquestionably came from the water used in diffusion. The water from the Leavitt well was found to contain 0.0024 per cent., or 24 parts per 100,000 of oxide of iron.

Quite recently a sample of lime removed from the kiln by Superintendent H. Schmode was subjected to analysis and found to be radically different in composition from the first sample analyzed. The results of this analysis are here given:

	Per cent.
Acid-insoluble matter	26.10
Acid-soluble silica	0.26
Lime (CaO)	63.44
Magnesia (MgO)	0.11
Alumina (Al_2O_3)	3.97
Iron oxide (Fe_2O_3)	2.09
Carbon dioxide (CO_2)	3.05
Sulphuric acid (SO_3)	0.14
Undetermined	0.84
	100.00

There is certainly sufficient iron oxide shown in this sample to have caused all the disturbances noted. These two analyses would indicate a decided lack of uniformity of composition in the lime rock used at the factory.

To sum up the whole matter, it is my opinion that the coloring of the sugar in the massecuite was due to iron oxide. The source of this iron is still an open question, but the evidence at hand points rather clearly to the lime rock as the origin of it.

The author wishes to express his gratitude to Prof. H. H. Nicholson, as the investigation has been carried on in the chemical laboratory of the University of Nebraska by his permission.

SOME CHEMICAL CONSTANTS OF FOSSIL RESINS.[1]

BY R. A. WORSTALL.

Received June 24, 1903.

WHILE the literature relating to the resins in general is quite extensive, it is nevertheless true that published data, in regard to

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[1] Read before the International Congress of Applied Chemistry at Berlin, June, 1903.

the chemical constants of those fossil and semi-fossil resins which enter into the composition of varnishes, are quite scarce. Several investigators[1] have published results obtained from specimens of a few of these resins, but their results are in general of little or no value for various reasons. In the first place, many authors have not taken pains to properly classify the particular resins with which they were working. Then, too, their work has in many cases been with single specimens and not sufficient data are available for any one resin from which definite conclusions may be drawn. Last, but not least, as K. Dieterich has pointed out in his excellent book upon the analysis of resins,[2] the methods employed for resins in general have not been either accurate or uniform. Almost without exception the methods for the analysis of fats have been applied to the resins—a class of compounds entirely different from the fats in origin and constitution, so that we have ester values of resins which contain no esters, direct acid numbers which are far too low, and a general lack of concordance in the results.

It is chiefly due to Tschirch and his pupils that we have a clearer idea as to the origin and chemical constitution of the resins, while to K. Dieterich we owe quite as much from the analytical point of view. The later, in the book previously referred to, has given us suitable methods of analysis for each resin, and applied these methods in determining the constants of many species. The work herein recorded was undertaken to extend our information concerning the fossil and semi-fossil resins—the so-called "Copals"—a subject to which Dieterich has given but brief attention,—with the hope of developing a rational scheme of analysis. Each specimen was taken from large shipments, and represents a fair average sample of a definite commercial grade. As many different specimens as it was possible to secure were examined, in the belief that from a large number of data better conclusions could be drawn. As descriptions of the physical properties and characteristics of these various resins are to be found in several books treating of such subjects, it has seemed best to omit all such data from consideration in this article, giving for each resin no more description than is necessary to properly classify it.

KAURI COPAL.

Kauri resin, or Kauri copal, a semi-fossil, was originally an

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[1] For a complete bibliography of this subject see "Die Harze und die Harzebehälter," by Tschirch.

[2] "Analyse der Harze, Balsame, und Gummiharze."

exudation from the pine tree of New Zealand—*Dammara Australis*—and is found only in the province of Auckland in open bush land from which the original forests have disappeared. In other parts of the colony, forests of these trees still exist which yield, on tapping, a soft spongy sap, while an intermediate quality of a semi-matured state—"bush Kauri"—also exists, which time might convert into semi-fossil variety. The data herein given refer entirely to the semi-fossil resin. The quantity of Kauri consumed annually in the United States more than equals that of all the other fossil and semi-fossil resins combined.

ACID NUMBERS.

In determining the acid numbers of Kauri the indirect method of Dieterich was followed, with a modification in the solvents used. One gram of the finely powdered resin was weighed out into a glass-stoppered bottle, and 15 cc. benzene and 5 cc. alcohol were added. Solution is complete in a few minutes with these solvents. Then 15 cc. of fifth-normal alcoholic potash were run in, the bottle tightly stoppered and allowed to stand eighteen hours, 25 cc. of alcohol then added and the excess of alkali titrated back with fifth-normal sulphuric acid, using phenolphthaleïn as an indicator. The method gives sharp end-reactions and closely agreeing duplicates. Blank determinations were run each time, using the same quantities of solvents.

As Dieterich has pointed out, direct titration gives acid values far too low for all resins, because the complete neutralization of the resin acids proceeds slowly. To illustrate this point the following experiment will serve. Several portions of a sample of Kauri, whose acid number had been accurately determined as 103, were weighed out and the acid number determined by indirect titration at different intervals of time. The results were as follows:

Time.	Acid number.
5 minutes	82
1 hour	92
3 hours	96
6 "	101
12 "	102
18 "	103

It is very necessary, as Dieterich has also observed, that rather strong acid be employed for the titration, as the addition of much water hydrolyzes the potassium salts and lowers the apparent acid number. The author has found the addition of alcohol before the titration a great help in securing sharp end-reactions.

At the very beginning of this work it became evident that there was a wide divergence between the acid values of different samples of Kauri, ranging from a minimum of 72 to a maximum of 142, the large lumps ("bold" gum) having always the lowest acid values, the fine chips and dust the highest. Dieterich, who had noted with other resins, especially dammar, that the dust had much higher acid numbers than the large lumps, at once concluded that this must be due to adulteration of the dust with colophony. But as all the resins herein described were taken from original packages which had not been opened since leaving Auckland, the author was convinced that no adulteration was possible.

Dieterich has condemned the iodine and bromine numbers as of no value when applied to resins, and has omitted those determinations in his schemes of analysis. That he is entirely mistaken—at least in so far as the Copals are concerned—will appear from the following results. Proof that these Kauri samples were not adulterated was afforded at once when the iodine values were determined. The latter ranged from a maximum of 170 to a minimum of 74, the iodine value being always at a *maximum* when the acid number was at a *minimum*, and decreasing directly as the acid number increased. As colophony has an acid number of 160 and an iodine value of 170, adulteration with the latter would have caused a simultaneous increase in both acid and iodine values.

In determining the iodine value, the usual Hübl method was employed, using a large excess of iodine solution, and allowing to stand eighteen hours before titrating.

The following table shows the results obtained from forty-three specimens of Kauri resin.

Number.	Description.	Acid.	Iodine.
1	XXXX White, large lumps	72	170
2	XX Brown, " "	72	154
3	X White, " "	72	162
4	Brown one, " "	77	140
5	X Brown, " "	77	160
6	X Nubs, white, large	76	154
7	XX " " "	76	159
8	No. 1 " " "	85	146

Number.	Description.	Acid.	Iodine.
9	X Nubs, brown, large	87	148
10	No. 1 " white, "	87	144
11	No. 1 " " "	87	149
12	No. 1 " " "	91	142
13	Chips, white, large	80	153
14	" " "	82	159
15	" " "	79	151
16	" brown "	86	162
17	" light, medium	96	143
18	" " "	99	143
19	" " "	92	137
20	" " "	97	140
21	" " "	95	137
22	" brown, "	89	132
23	" light, small	112	115
24	" dark, "	113	110
25	" and dust	111	115
26	Small brown chips	92	124
27	Bright fine chips	103	120
28	" " "	103	125
29	" " "	107	113
30	" seeds	107	113
31	Medium "	103	113
32	" "	108	111
33	" "	122	105
34	" "	123	105
35	" "	122	107
36	Dark "	125	95
37	Bright dust	118	105
38	" "	120	105
39	Medium "	127	93
40	" "	130	87
41	" "	123	82
42	Brown "	133	89
43	" "	142	74

While no particular relation could be expected to exist between two arbitrary values such as the acid numbers and the iodine absorption, it is worth noting that the sum of these two values is approximately a constant. For the forty-three specimens the average of this sum is 228, the maximum being 248 and the minimum 205. And if for each specimen the percentage of impurities is taken into consideration and these values estimated for the pure resin contained, the divergence is less marked. In other words, the iodine number decreases in almost exact proportion as the acid number increases, and *vice versa*.

From the researches of Tschirch and his pupils, it appears that the copals consist of "resenes"—neutral compounds containing oxygen and possibly of aldehyde nature— and of the resin acids. Other investigators[1] have noted the fact that the copals will absorb oxygen, and evidently the increase in acid number and decrease in iodine absorption is due to oxidation of these "resenes," by contact with the air, to resin acids, and that heretofore the finer the particles of the resin and the more porous they are, the higher will be their acid number. That this increase in the acid number is actually due to oxidation, the following experiments will illustrate.

A number of samples of Kauri were selected, each one finely powdered, and its acid and iodine numbers determined. These samples were then left four months in open bottles exposed to the air, and the powdered resins stirred from time to time to promote oxidation. At the end of this time their constants were again determined with the following results:

	Before oxidation.		After oxidation.			
Number.	Acid.	Iodine.	Acid.	Iodine.	Acid. Increase.	Iodine. Decrease.
1	72	154	87	133	15	21
2	76	159	111	121	35	38
3	77	140	93	115	16	25
4	72	170	107	110	35	60
5	97	109	104	99	7	10
6	105	113	109	112	4	1

Samples 1, 2, 3 and 4 were hard, "bold" gum of highest quality, while samples 5 and 6 were of a soft, spongy, lowest grade Kauri, in which oxidation had already made much progress before the experiment was carried out.

This oxidation proceeds rapidly in presence of alkalies, so that open saponification with alcoholic caustic potash gives acid numbers that are much too high. Doubtless this fact, in connection with the impossibility of obtaining correct acid numbers by direct titration, has led to the reporting of ester values in resins where no esters exist. That Kauri is free from esters was shown by saponifying several samples in flasks with return condensers, digesting for one hour on the steam-bath. In every case the saponification number thus found was the same as the indirect acid number.

[1] See Kiessling, Weger, and Lippert : *Chem. Rev.*, **98**, I, 286 ; *Ztschr. angew. Chem.*, **98**, I, 1248.

MANILA COPAL.

This semi-fossil resin comes from the islands in the Malay Archipelago. Its botanical source is unknown. Commercially it is second to Kauri in the amount consumed each year in the United States for varnishes. Nineteen samples were taken from direct importations, the acid and the iodine values being determined by the same methods employed for Kauri, with the following results:

Number.	Description.	Acid.	Iodine.	Sum of acid and iodine.
1.........	Finest white, "bold"	146	148	294
2.........	Medium " "	167	128	295
3.........	" " "	175	132	307
4.........	Hard brown "bold"	176	131	307
5.........	White Nubs	165	135	300
6.........	Medium white Nubs	176	125	301
7.........	Amber Nubs	180	125	305
8.........	White chips	176	127	303
9.........	" "	178	131	309
10.........	Medium chips	180	129	309
11.........	" "	180	125	305
12.........	Amber chips	182	119	301
13.........	" "	182	117	299
14.........	" "	186	119	305
15.........	" "	187	120	307
16.........	" "	187	116	303
17.........	" "	188	119	307
18.........	" "	190	120	310
19.........	Dust	199	104	303

It will be noticed that the sum of the acid and the iodine values is in each case quite near the average, 304, and that the less marked increase in acid values as the size of the gum decreases indicates that oxidation by the air is not so rapid as in the case of Kauri. The effect of oxidation was determined just as for Kauri by allowing the finely powdered resin to stand in contact with the air for four months. The following table shows the results:

		Before oxidation.		After oxidation.	
Number.	Description.	Acid.	Iodine.	Acid.	Iodine.
1.......	Hard brown, "bold"	176	131	183	128
2.......	" white, "	142	148	146	144
3.......	White chips	186	119	189	113
4.......	Medium chips	180	125	191	112
5.......	" white, "bold"	175	132	178	122
6.......	" " "	167	133	178	128

Oxidation, therefore, does not proceed as rapidly or as far with Manila as with Kauri. Open saponification, however, gives too high results. Closed saponification gives the same figures as the indirect acid numbers, showing the absence of esters.

PONTIANAC COPAL.

One of the most recently exploited copals is the so-called "Pontianac," a semi-fossil from the Malay archipelago. In many ways it seems to be a connecting link between Kauri and Manila, not only in its physical characteristics, but also in its chemical constants. At present the consumption of the resin in the United States is in an experimental stage, and only two samples were available.

		Before oxidation.		After oxidation.	
Number.	Description.	Acid.	Iodine.	Acid.	Iodine.
1	Medium chips	135	142	153	104
2	Small "	143	119	157	102

It will be noted that its acid and iodine values lie between those of Kauri and Manila, and that it is more easily oxidized than Manila, but not so readily as Kauri. In its physical properties it more closely resembles Manila. It contains no esters.

SOUTH AFRICAN FOSSIL COPALS.

Zanzibar, Madagascar and Mozambique copals, the hardest and probably the most ancient of the fossil copals, are all found on the southeast coast of Africa. The botanical source of Zanzibar copal is probably the trachylobium verrucosum, and it is probable that the other two varieties of resin come from closely related species. Zanzibar is still of commercial importance, but Madagascar and Mozambique are but little used in the United States.

The acid numbers, iodine absorptions, and effect of oxidation were determined for these resins just as for those previously described.

		Before oxidation.		After oxidation.	
Resin.	Description.	Acid.	Iodine.	Acid.	Iodine.
Zanzibar	Prime white "sorts"	79	123	79	123
"	Amber chips	104	115	102	114
Mozambique	White "sorts"	80	136	107	108
Madagascar	Amber "sorts"	95	126	100	106

Zanzibar does not seem to be readily oxidized. None of these resins contained esters.

WEST AFRICAN FOSSIL COPALS.

Of the west African copals, the following were examined: "North Coast" or "Akra," red and white Angola, Congo and Benguela. The botanical source of these resins is not known positively. The following table gives the results:

		Before oxidation.		After oxidation.	
Resin.	Description.	Acid.	Iodine.	Acid.	Iodide.
North Coast	White, "bold"	108	143	127	109
" "	" "	109	143	125	122
" "	" "	116	140	137	116
Benguela	" "	139	142	161	121
Congo	" "	150	122	150	116
"	No. 2 "	152	122	153	109
Red Angola, select		143	130	142	115
White " "		127	136	128	118

It may be remarked that the effect of oxidation upon all resin described in this paper was studied in the same manner as for Kauri, by leaving the finely powdered resin in contact with the air for four months. It is worth noting that while oxidation does not increase the acid numbers of Congo or the Angolas, it materially decreases the iodine absorption. The reason for this is not clear. None of these copals contain esters.

SIERRA LEONE COPAL.

Sierra Leone copal is the exudation from the bark of the *Copaifera Guibourtiana,* on the west coast of Africa. This tree flourishes in the elevated mountainous districts. The gum is gathered as an annual crop, thereby differing from most of the other varnish resins. The annual gathering takes place about the end of March, the bark being extensively cut and slashed, and the gum which flows from these incisions being afterwards collected. This resin hardens rapidly. The supply has been steadily decreasing and the cost, in consequence, rapidly increasing, so that Sierra Leone is not now used to a very great extent in the United States.

Two samples were examined with the following results:

		Before oxidation.		After oxidation.	
Number.	Description.	Acid.	Iodine.	Acid.	Iodine.
1........	Finest select No. 1	118	105	116	105
2........	No. 2 grade	114	102	116	108

It therefore appears that Sierra Leone is not readily oxidized. Hot saponification showed absence of esters.

BRAZILIAN COPAL.

Brazilian copal is a semi-fossil resin of uncertain botanical source from South America. Three samples were examined with the following results:

		Before oxidation.		After oxidation.	
Number.	Description.	Acid.	Iodine.	Acid.	Iodine.
1	Fine "bold" yellow	131	123	138	116
2	" " white	143	134	150	119
3	" " "	149	125	158	116

DAMAR.

While Damar is neither a fossil nor semi-fossil resin, and hence not strictly included under the title of this paper, its importance in varnish-making is such that it seems well to include it in consideration. The white damars used in the manufacture of varnish are commercially of three varieties—the Batavian from Java, and the Singapore and Padang from Sumatra. They are all exudations of *Dammara Orientalis,* the trees being cut periodically for the gum.

Eleven samples of white dammar were examined with the following results:

Number.	Description.	Acid.	Iodine.
1	Select Padang	24	116
2	" Singapore	55	104
3	" Batavian	24	124
4	No. 1 "	24	117
5	" 2 "	41	116
6	" 2 "	41	115
7	Batavian siftings	50	108
8	" "	50	107
9	" dust	51	104
10	" "	47	106
11	" "	50	103

The acid numbers were determined just as for all the preceding resins, using the same solvents. The decrease in the iodine absorption as the acid number increases shows that oxidation occurs with damar just as with the other resins. Hot, open saponification gives too high acid numbers for the same reason. Had Dieterich determined the iodine numbers of the damar dusts whose acid numbers he found high, he probably would not have concluded that the dusts were adulterated with colophony.

It would seem to the author that, in view of the results obtained, the value of the iodine absorption method as applied to the varnish resins is fully established. The almost universal tendency of the resins to oxidation when in contact with the air, as also brought out by this work, and the consequent wide range in acid and iodine values, makes it evident that chemical comparison of different samples of any resin are of value only when the samples to be compared are of the same general nature—in other words, it will not do to compare "bold" gum with "chips," or "Nubs" with "dust," for the reason that the finer the particles of gum, the farther the oxidation has progressed. But when it is desired, for the sake of greater accuracy, to supplement physical tests or inspection by chemical analysis, the author has found the following scheme of analysis accurate and reliable, *provided* it is used comparatively, that is, to test "dust" against "dust," "chips" against "chips," etc.

Moisture.—The resin is finely powdered and 1 gram dried for one hour at 110° C. on a watch crystal.

Insoluble Matter.—Two grams of the finely powdered resin are weighed out into a small beaker, and 25 cc. benzene and 10 cc. acetone added. Solution is complete for the softer resins in a few minutes, and slow for Zanzibar and the other harder resins. When necessary, solution of the latter may be effected in épichlorhydrin, aniline, or other more active solvent. When the solution is complete, allow to settle until clear, and decant the clear liquid, but *not* through the filter as it would clog the paper. Add more of the solvents to the residue in the beaker, and wash onto a filter-paper, previously washed out, the same solvents dried and weighed. Wash the residue clean, dry and weigh as total insoluble matter.

Ash.—Ignite paper and contents until white, and weigh residue as ash.

Insoluble Organic Matter.—The difference between the total insoluble matter and the ash represents the insoluble organic matter—bark and vegetable débris.

Indirect Acid Number.—Weigh out 1 gram of the finely powdered resin into a glass-stoppered bottle, add 15 cc. benzene, 5 cc. alcohol and 15 cc. fifth-normal alcoholic caustic potash. Allow to stand tightly stoppered for eighteen hours, add 25 cc. alcohol, a few drops phenolphthaleïn, and titrate back with fifth-normal sulphuric acid. The number of milligrams of potassium hydroxide used represents the acid number.

Iodine Absorption.—Weigh out 0.2 gram of the finely powdered resin into a glass-stoppered bottle and add 10 cc. chloroform. Add 40-50 cc. of Hübl's iodine solution, allow to stand eighteen hours, then titrate back with thiosulphate.

Color.—Dissolve 10 grams of the resin in 100 cc. of a mixture of half benzene and half acetone, allow to stand in a 4-ounce oil vial until it has settled bright, then compare the colors of the clear solutions.

The above methods, when applied to the comparison of similar grades of the same resin, give surprisingly accurate results. Other things being equal, a higher percentage of insoluble organic matter, which would char in the kettle and darken the melt, or a higher acid number and lower iodine value, which would show more complete oxidation and hence indicate a more porous structure in the resin, or a darker color in solution, indicating a corresponding darker color when melted—these are the points which condemn a sample.

In conclusion, the author would state that he hopes soon to extend this investigation to the melted copals—especially to study the oxidation of the same, which may have important bearing on the durability of varnishes made from these resins.

CHICAGO VARNISH CO.,
CHICAGO, March, 1903.

ON THE RELATION OF THE SPECIFIC GRAVITY OF URINE TO THE SOLIDS PRESENT. SECOND PAPER.

BY J. H. LONG.

Received June 18, 1903.

SOME months ago[1] I gave the results of experiments carried out on the determination of the relation between the total solids of urine and the specific gravity at 25° C. A factor was found here corresponding to the coefficient of Haeser, but considerably larger than the number usually given, on account of the higher temperature at which the specific gravities were observed.

It seemed desirable to separate the effect of sodium chloride in fixing this relation, inasmuch as this substance is not a product

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[1] This Journal, **25**, 257.