

**PROXIMATE ANALYSIS OF SPENT ALKALINE LIQUOR
FROM THE REDUCTION OF POPLAR WOOD FOR
PAPER STOCK, BY THE SODA PRO-
CESS, WITH A DESCRIPTION
OF THE METHOD.**

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SO far as I know, no attempt at analysis of this complex liquid has ever been made, and I know of no references in literature relating to its composition. I have, at different times, made determinations of some of the constituents of this liquor, particularly the total alkali and acetic acid, but this is my first attempt at an investigation of the proximate constituents. The reason why the subject has not been taken up by technical chemists, employed in the paper industry, is because of the complex nature of this waste and the fact that manufacturers have had no idea that it contained anything valuable which they could recover except the alkali, for which greatly improved machinery has been contrived during the past fifteen years.

My interest in this subject was much increased by the action of the Scottish Paper Makers Association, which nearly two years ago offered prizes for the investigation of various waste products resulting from their paper industry, among which was the waste alkaline esparto liquor.

The subject is brought before you now simply in introductory form, but still in a way which I trust will be of some interest and value.

THE PROCESS BY WHICH THE SPENT LIQUOR RESULTS.

We are told that M. Meliner, a Frenchman, in 1865, was the first to discover the process of reducing spruce and poplar woods to paper stock by treatment with alkalies under steam pressure. The process now consists in cutting the wood into chips, the fiber of which is about $\frac{1}{2}$ inch long, and charging same into digesters holding from 3 to 5 cords. Strong sodium hydroxide liquor, containing from about 90 to 100 grams of soda-ash per liter, is then furnished to an amount of about 4 gallons to each cubic foot of capacity of the digester. Steam pressure of 100 to 120 pounds is then applied for from seven to eight hours, when the

mass is blown out under pressure and washed. This alkaline liquor, with the extracted matter, is the subject for our consideration. Before it is exposed to the air, it has a light rose tint, but afterward becomes black instantly. As it comes from the digester, it has a specific gravity of about 1.08 (or $10\frac{2}{3}^{\circ}$ Bé.) at 15° , and contains 14 to 15 per cent. of total solid matter at 100° , which is very deliquescent.

No attempt at recovering any useful products other than soda-ash has ever been made by those employed in the paper industry, and I doubt if any products as valuable as the ash could be obtained unless it included it. Neither could other valuable products be sought at the expense of the alkaline carbonates.

I submit the following proximate analysis of this liquor. The results are given on the basis of total solids dried at 100° :

	Per cent.
Silica.....	0.11
Iron and aluminum oxides.....	0.02
Calcium oxide.....	0.05
Magnesium oxide.....	0.00
Potassium oxide.....	0.69
Sodium oxide.....	25.69
Carbon dioxide.....	3.43
Absolute acetic acid.....	9.89
Organic matter extracted by naphtha, boiling under 60°	1.56
Ether.....	7.14
Absolute alcohol.....	28.26
Water.....	17.02
Total alkalis estimated with normal acid by incineration of the evaporated liquor...	44.25

No attempt is made at combining the acid substances with the bases, though, of course, we know that the carbonic and acetic acids, also the acid resinous substances, are combined with the small amounts of mineral bases, and the alkalis. The remaining 6 per cent. is not definitely accounted for. It is probably all water, largely contained in the sodium hydroxide remaining after saturating all the acid substances, and not accounted for above, and a little water not driven off at 100° .

We know that a large fraction of the total organic matter possesses acid properties, since approximately 18.59 per cent. of the total solids, or 34.43 per cent. of the total organic matter may be precipitated with a slight excess of sulphuric acid at a temperature

of about 40° . This temperature was found best adapted for the precipitation and the washing of the precipitate. At much higher temperatures, the resinous substances will melt, and are more soluble in the menstruum from which they are precipitated. By neutralizing with normal hydrochloric acid, 17.96 per cent. was precipitated.

I hope to be able to investigate chemically and for technical uses, the nature of these acid resinous substances, and present the results at some future meeting.

The method employed for the organic part of this work is the system of solvents recommended by Dragendorff. A quantity of the liquor was contained for use in a tight jar. The total solids were first determined, so that when, for the purpose of different determinations, a definite volume was taken, the solids could be calculated without the trouble of weighing.

In order to prepare a sample suitable for the process of extraction successively by solvents, 5 cc. of the liquor, just neutralized with normal sulphuric acid, were absorbed upon an Adams' paper coil and placed in an extraction thimble for convenience, and dried thoroughly at 100° . The coil was then extracted with naphtha, boiling under 60° in a Soxhlet tube, and the extracted matter determined in the usual way. After the evaporation of this solvent, the coil was successively extracted with ether and absolute alcohol in the same manner. The extract by water contained not only all the organic matter soluble in it, but all the mineral constituents, as sulphates, with the possible exception of traces of silica.

From this extract the organic matter was determined by burning off, and from the mineral portion the alkalies were estimated. The total acetic acid was determined by taking 100 cc., acidifying with slight excess of sulphuric acid, and distilling with the addition of fresh portions of water, until the total distillate amounted to 1 liter. This was distilled a second time to the same volume and the distillate was thoroughly tested for the presence of acetic acid and no other, which was then determined from an aliquot part with tenth-normal sodium hydroxide.

The mineral analysis was made by evaporation and incineration of a fresh sample of 25 cc. in the usual way.

It is the purpose of the writer to pursue this investigation further by taking the extract by each solvent and differentiating it

as far as possible into its separate constituents in the hope that the results may be of some interest, though having no commercial value. The author will be glad to have the subject discussed by the Society, and thankful for any criticisms or suggestions regarding the work.

DOES "ARGEMONE MEXICANA" CONTAIN MORPHINE ?

BY J. O. SCHLOTTERBECK.

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MEXICAN or prickly poppy, as this plant is more familiarly known, is native to the southern states of North America, Mexico, and the West Indies, but it has spread to the north and has also been accidentally introduced by trading ships into distant tropical and subtropical lands to such an extent that it has become a troublesome weed in some localities. The plants are easily propagated from seeds which have for some time been offered by seedsmen for ornamental planting, consequently the prickly poppy has become rather cosmopolitan. The plant is striking in appearance, attains a height of 2 feet, is erect, bristly, and glaucous. The leaves are alternate, sessile, sinuately lobed, armed at the margin and under surface with very sharp prickles. The upper surface of the leaves is beautifully blotched with white. The solitary flowers are yellow, about $1\frac{1}{4}$ inches broad, possessing a soft, bristly ovary with 4 to 6 red-tipped stigmas. When about to delisce, to discharge the numerous finely pitted black seeds, the prickly capsule turns from green to brownish-black. When bruised, all parts of the growing plant exude a yellow, milky juice which is acrid, bitter, and of penetrating odor.

The Spanish claim emetic properties for the seeds and purgative properties for the fixed oil therefrom. Others believe the plant to possess narcotic qualities. The juice of the leaves has gained a reputation among the laity, at least, in the treatment of opacities of the cornea, pain of cephalalgia and inflammation of the eyes. Prickly poppy is official in the "Mexican Pharmacopoeia," and while reports upon its therapeutic value are very contradictory and at times fabulous, its importance has merited detailed notice of its properties and uses in the dispensaries of the United States. Considering the repute in which this plant has been held as a remedial agent among Spanish-American peoples it is rather remarkable that so little attention has been directed to its chemical study.