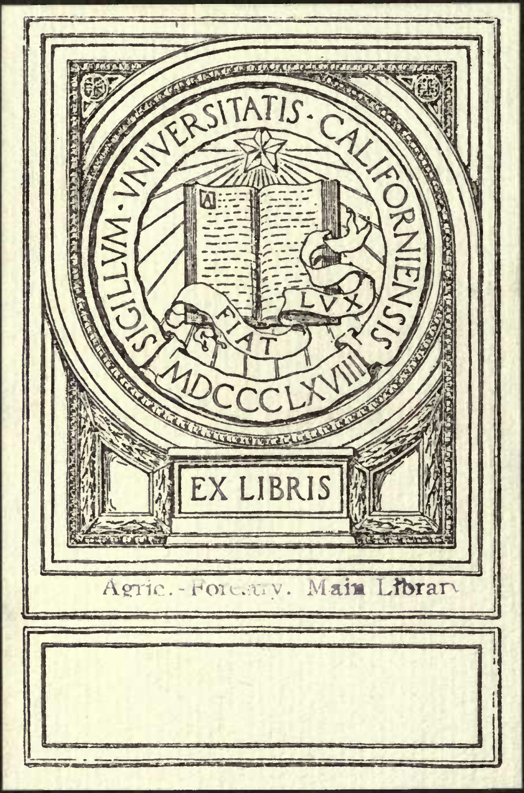
UTILIZATION OF WASTE SULPHITE LIQUOR.
Canadian Forestry Bulletin 66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DEPARTMENT OF THE INTERIOR, CANADA
Hon Arthur Meighen, Minister ; W. W. Cory, Deputy Minister
FORESTRY BRANCH—BULLETIN No. 66
R. H. Campbell, Director of Forestry

UTILIZATION OF WASTE SULPHITE LIQUOR

OTTAWA
J. de LABROQUERIE TACHÉ
PRINTER TO THE KING'S MOST EXCELLENT MAJESTY
1919
49120—1 *Price 50 cents.*

DEPARTMENT OF THE INTERIOR, CANADA
HON. ARTHUR MEIGHEN, Minister; W. W. CORY, Deputy Minister
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R. H. CAMPBELL, Director of Forestry

UTILIZATION
OF
WASTE SULPHITE LIQUOR

A REVIEW OF THE LITERATURE
COMPILED BY
Dr. BJARNE JOHNSEN and R. W. HOVEY, B.Sc.
OF THE
DIVISION OF PULP AND PAPER

FOREST PRODUCTS LABORATORIES OF CANADA
Montreal
DR. J. S. BATES, Superintendent

OTTAWA
J. DE LABROQUERIE TACHÉ
PRINTER TO THE KING'S MOST EXCELLENT MAJESTY
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49120—1

4/6/21

CONTENTS

ABBREVIATIONS

Allgem. Fischerei Ztg.=Allgemeine Fischerei Zeitung
Ann.=Annalen der Chemie
Arbeit. Kais. Gesundh.=Arbeiten aus dem Kaiserlichen Gesundheitsamte
Bé.=Baumé
Ber.=Berichte der deutschen chemischen Gesellschaft
Ber. botan. Ges.=Berichte der deutschen botanischen Gesellschaft
Ber. pharm. Ges.=Berichte der deutschen pharmzeutischen Gesellschaft
Biedermanns Zentr.=Biedermanns Zentralblatt fur Agrikultur Chemie und rationellen Landwirtschaftsbetrieb
Biochem. Z.=Biochemische Zeitschrift
*Chem. Abs.=Chemical Abstracts
*Chem. Eng.=Chemical Engineer
Chem. Ind.=Die Chemische Industrie
Chem. Techn. Neuzeit.=Chemische Technologie der Neuzeit
Chem. Techn. Ztg.=Chemiker und Techniker-Zeitung
Chem. Trade J.=Chemical Trade Journal and Chemical Engineer
Chem. Zeitschr.=Chemische Zeitschrift
Chem. Zentr.=Chemisches Zentralblatt
Chem-Ztg.=Chemiker-Zeitung
Collegium (Official organ of the Int. Assn. of Leather Trades Chemists)
Comp. rend. soc. biol.=Comptes rendus hebdomadaires des séances de la société de biologie
Compt. rend. trav. lab. Carlsberg=Comptes rendus des travaux du laboratoire de Carlsberg
Compt. rend.=Comptes rendus hebdomadaires des séances de l'académie des sciences
Deut. Gerber Ztg.=Deutsche Gerber Zeitung
Deut. Techn. Ztg.=Deutsche Techniker Zeitung
Deut. Zuckerind.=Die Deutsche Zuckerindustrie
D. Landw. Presse.=Die Landwirtschaftliche Presse
Dingler's polytech. J.=Dingler's polytechnisches Journal
Engineer=The Engineer
Eng. Mining J.=Engineering and Mining Journal
*Eng. Record=Engineering Record.
Farber-Ztg.=Farber-Zeitung (Zeitschrift fur Farberei Zengdruck und den gesamten Farbenverbrauch)
Farben-Ztg.=Farben-Zeitung
Gerber=Der Gerber
Gesund.-Ing.=Gesundheits-Ingenieur
Jahrb. Chem. Techn.=Jahrbuch der Chemischen Technologie
J. Am. Leather Chem. Assoc.=Journal of the American Leather Chemists Association
J. Gasbel.=Journal fur Gasbeleuchtung
*J. Ind. Eng. Chem.=Journal of Industrial and Engineering Chemistry
*J. Soc. Chem. Ind.=Journal of the Society of Chemical Industry
Kolloid-Z.=Kolloid-Zeitschrift
Kunststoffe=Kunststoffe
Landw. Ztg.=Landwirtschaftliche Zeitung
Leather World=Leather World
Ledertechn. Rundschau=Ledertechnische Rundschau
*Met. Chem. Eng.=Metallurgical and Chemical Engineering
Mitt. Prufungsamt Wasser u. Abwasser=Mitteilungen aus deu Prufungsamt fur Wasser und Abwasser
Mitt. Techn. Gew. Mus.=Mitteilungen aus dem Technischen Gewerbe Museum
Mon. Pap.=Moniteur Papeterie
Mon. sci.=Moniteur scientifique du Docteur Quesneville
Oesterr. Chem.-Ztg.=Oesterreichische Chemiker-Zeitung
Oil, Paint Drug Rep.=Oil, Paint, and Drug Reporter
*Paper=(The weekly journal published in New York).
Paper-Maker Brit. Trade J.=Paper-Maker and British Trade Journal
Paper Makers' Monthly J.=Paper Makers' Monthly Journal
Paper Making=Paper Making
Paper Trade J.=Paper Trade Journal
Papier-Fabr.=Papier-Fabrikant

ABBREVIATIONS—*Concluded.*

Papier-Ztg.=Papier-Zeitung
*Papir J.=Papir Journalen
*Pulp Paper Mag. Can.=Pulp and Paper Magazine of Canada
Rauch Staub.=Rauch und Staub
Rev. gen. mat. color.—Revue générale des matières colorantes de la teinture de l'impression et des apprêts
Seifensieder-Ztg.=Seifensieder-Zeitung und Revue uber die Harz-Fett-und-Oelindustrie
Svensk Kem. Tid.=Svensk Kemisk Tidskrift
Svensk Pap. Tid.=Svensk Pappers Tidning
Tekn. Tid.=Teknisk Tidskrift
Technikum=Technikum des Ledermarkt
Tid. Kemi. Farm. Terapi=Tidskrift for Kemi Farmaci Terapi
Wasser Abwasser=Wasser und Abwasser
Water Supply Papers=Water Supply Papers of the U. S. Geological Survey
*Wochbl. Papierfabr.=Wochblatt fur Papierfabrikation
World's Paper Trade Rev.=World's Paper Trade Review
Z. angew. Chem.=Zeitschrift fur angewandte Chemie
Zentr. oesterr-ungar Papierind.=Zentralblatt fur die oesterr-ungar Papierindustrie
Z. Fischerei=Zeitschrift fur Fischerei
Z. Hyg.=Zeitschrift fur Hygiene
Z. Spiritusind.=Zeitschrift fur Spiritusindustrie
Z. Ver. Zuckerind.=Zeitschrift des Vereins der deutschen Zucherindustrie
Z. ges. Wasserwirtsch.=Zeitschrift fur die gesamte Wasserwirtschaff
Z. ges. Textilind.=Zeitschrift fur die gesamte Textilindustrie
Z. Nahr. Genussm.=Zeitschrift fur Untersuchung Nahrsungsund Genussmittel sowie Gebrauchs-egegenstände

The above journals marked with an * have been abstracted in the Forest Products Laboratories.

UNITS

1 centimetre (cm.)=0.393 inches
1 square centimetre (sq.cm.)=0·155 square inches
1 cubic centimetre (c.c.)=0·061 cubic inches
1 metre (m.)=39.37 inches=3·28 feet
1 square metre (sq.m.)=1550 square inches=10·763 square feet
1 cubic metre (cub.m.) (1000 litres)=35·289 cubic feet=1.3079 cubic yards
1 kilometre (km.)=3280·8 feet=0·621 miles
1 square kilometre (sq.km.)=0.386 square miles=247·1 acres
1 hectare=2·471 acres=11595·9 square yards
1 gramme (g.)=0.035 ounces (av.)=0·0022 pounds (av.)
1 kilogramme (kilo or kg.)=35·274 ounces (av.)=2·204 pounds (av.)
1 metric ton (1000 kilogrammes)=2204.62 pounds (av.)=1·102 short tons=0·984 long tons
1 litre(l.)=0·2199 gallons (Imp.)=61.023 cubic inches=0.0353 cubic feet
1 hectolitre (hl.)=3.531 cubic feet.

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1 inch (in.)=2·54 centimetres
1 square inch (sq.in.)=6.45 square centimetres
1 cubic inch (cu.in.)=16·387 cubic centimetres
1 foot (ft.)=30·48 centimetres
1 square foot (sq.ft.)=929 square centimetres=0.0929 square metres
1 cubic foot (cu. ft.)=28·317 litres
1 mile (mi.)=1.609 kilometres
1 square mile (sq. mi.)=640 acres=2·59 square kilometres
1 acre=43560 square feet=0·001562 square miles=0.4046 hectares=4046·87 square metres
1 Imperial gallon (gal.)=1·2009 gallons (U.S.)=277.41 cubic inches=4.5459 litres
1 ounce (oz.) (av.)=28.3495 grammes
1 pound (lb.) (av.)=453·59 grammes=0.45359 kilogrammes
1 short ton=2000 pounds (av.)=0.892857 long tons=907·185 kilogrammes=0.907185 metric ton
1 long ton=2240 pounds (av.)=1·12 short tons=1016.05 kilogrammes=1.01605 metric tons
1 cord (of wood)=128 cubic feet=3.624 cubic metres

UNITS—*Concluded.*

	Dollars
Great Britain	
1 penny (d)=	0.02
1 shilling (s.)=	0·24
1 pound (£)=	4·87
Germany	
1 pfennig (P)=	0.00238
1 mark (M)=	0.238
France	
1 centime (C)=	0·00193
1 franc (F)=	0·193
Norway and Sweden	
1 ore (O)=	0.00268
1 krona (Kr)=	0·268

PREFACE

The efforts in the direction of eliminating industrial waste by proper utilization of the raw material have in recent years drawn much attention to the utilization of the waste liquor from the manufacture of sulphite pulp. In Canada very little progress has been made towards the solution of this problem and no doubt one of the reasons for this is the lack of information with regard to what has already been accomplished along these lines. This is very natural when we consider that the data on this subject are distributed over an enormous field of literature, especially foreign literature. It is the object of this publication to condense all available information into a form in which it will be of the greatest usefulness to the industry as well as to those who wish to go into research work.

In 1910 M. Muller published a book in German "Die Literatur der Sulfitablauge" which contained references to German literature on this subject and on allied problems. A continuation of this work up to the end of 1913 was published by Muller in 1914 and both these publications have been of great service in the preparation of this bulletin. Considering that much of the literature referred to is not available at the present time and that most of the articles are only directly available at the large libraries, the most important abstracts have been made as complete as possible. The information has been conveniently arranged in chapters according to the nature of the recovered products and a short discussion has been added in the form of an introduction to each of the more important chapters.

In these discussions valuable information obtained from the various industries and from special authorities has been used, for which the authors wish to express their thanks. Acknowledgment is due to Prof. J. A. McRae of Queen's University who made a preliminary survey of a portion of this literature in the summer of 1915. The writers are also indebted to Mr. O. F. Bryant, chief of the Division of Pulp and Paper of the Forest Products Laboratories, for valuable assistance rendered in the preparation of this bulletin, and also to Mr. C. B. Thorne, of the Riordon Company, and Mr. G. F. Steele, of the Canadian Export Company, for the loan of files of technical journals.

BJARNE JOHNSEN.
R. W. HOVEY.

INTRODUCTION

The Canadian sulphite pulp industry consumed in 1916, 728,000 cords of pulpwood (see Forestry Branch Bulletin No. 62 B: Pulpwood, 1916). At least one-half of the dry weight of this wood or considerably more than 1,000 tons of wood substance, therefore, was contained in the waste sulphite liquor which was discharged every day from the mills as a useless waste. This figure is sufficient to show how significant it is for all wood-pulp producing countries to eliminate this waste of material by turning the valuable organic products contained in the liquor into valuable products. That the importance of a proper utilization of the waste liquor has been fully recognized is shown by the great number of references contained in this publication, the author register of which contains approximately 350 names of persons who have reported officially on this subject. But in spite of the large amount of work that has already been carried out in connection with this question and notwithstanding the fact that a few processes for the utilization of waste sulphite liquor have gained industrial importance in some countries, the problem is far from being solved. It can not be considered to be solved before a process or a combination of processes is established which will utilize all the substances in the liquor so that products will be derived therefrom in an economical way and in a quantity and quality which will enable them to compete with present products on the market.

The first difficulty in complete utilization of the liquor is presented by the fact that only about 40 per cent of the total liquor will drain off from the pulp without special arrangements for forced draining, and even with such equipment it would probably be difficult to recover more than 60 per cent. The remaining portions must be removed by water, which means a further dilution and therefore an appreciable increase of the volume, requiring large-sized apparatus for handling.

It is of great interest, therefore, to prevent a further dilution of the already very dilute liquor, as most of the processes of utilization call for a concentration of the liquor to a certain density. The fact that the economy of many of these processes largely depends upon the cost of evaporation, as the 10 tons of liquor obtained per ton of pulp contain only 11 to 12 per cent of solid substances, has made the question of evaporation one of the most important in the discussion of the waste sulphite liquor problem. Under "Evaporation" p. 162 references have been made to the various methods of evaporation which are as a rule carried out in connection with the simultaneous recovery of sulphurous acid, but it may be of interest here to point out a few principles of removing the excess of water, which are now in the foreground of the discussion of this point. One of the processes of concentration consists of atomizing the liquor at 100° C., which then in that form is mixed with the hot flue gases at about 270° C. The flue gases are thereby assumed to be cooled down to about 180° C., at which temperature one cubic metre of the gases should be capable of taking up and carrying off 1,000 grammes of water. The suitability of this principle for sulphite liquors is apparently not sufficiently known to be reported on here.

A new evaporator has recently been built by Soderlund-Boberg, which is claimed to give a most efficient utilization of the heat. The idea of this evaporator is to compress slightly the vapours from the liquor, whereby the temperature of these is raised a few degrees and the heat from the compressed warm steam can be used for the evaporation of further quantities of liquor. Finally, it is worth mentioning the removal of water by freezing as suggested by Oman for the Scandinavian countries with their comparatively cheap water power. The economy of this progress has not been reported on in detail.

Among the processes for utilization of waste sulphite liquor only a few are of immediate practical interest to Canada. The manufacture of tanning materials is one of these. The processes of manufacturing have already been reported on and also the suitability of this material for tanning purposes. It will only be mentioned here that Canada imports tannin extracts from sulphite liquor, at a price ranging from three-quarters of a cent to one cent per pound, which are used to a large extent in Canadian tanneries in the preparation of certain leathers, chiefly sole leather.

The use of sulphite waste liquor as a road and dust binder and as a binder for powdered materials such as peat would seem to be of importance to Canada.

The manufacture of ethyl alcohol from waste sulphite liquor is discussed on page 106 and the calculations, which are based upon the experience of operating sulphite spirit plants give a manufacturing cost of $0·185 to $0·32 per Imperial gallon, which is considerably less than the cost of production of alcohol from grain. This has been stated by Brecker (in J. Ind. Eng. Chem., vol. 9 (1917), p. 612), for 1916, to be about $0·48 per Imperial gallon, 90 per cent spirit in the United States, and has been estimated somewhat higher for Canada (about $0.60). The main question is, therefore, whether there is a sufficient market for this alcohol which without special purification contains certain impurities, especially menthyl alcohol (about 3 per cent). Recent investigations by the United States Geological Survey (1912) reported on in the United States Bulletin No. 392, and also experiments made in Europe, prove that the alcohol can be used with great advantage for motive power. United States Bulletin No. 392 contains details of this point and in Hagglund's book on Alcohol from Waste Sulphite Liquor, referred to on page 122, an interesting discussion of this problem is contained. It has been found that in motors of special construction a very efficient utilization of heat is obtained. This is at least the case with stationary motors of low speed (not above 300 revolutions per minute) which can give a heat efficiency of 33 per cent in the case of spirit motors, while the heat efficiency in benzine motors as a rule is about 23 per cent. This good result is obtained only when the compression ratio of 10 to 1 is used in the alcohol motor against 4 to 1 with the benzine motor and when cooling water of a suitable temperature, namely about 100°C., is used. But this special alcohol motor with high compression cannot be used for high speed motors in vehicles, and it is a decided drawback that the alcohol motor cannot be used for benzine, without alterations. The usual benzine motor can, however, be operated with alcohol if slight alterations are made with the carburetting device in order to obtain the most favourable proportion of the air-alcohol mixture. The efficiency is considerably increased if the air is preheated by utilizing the heat in the exhaust of the motor. One disadvantage is presented in regard to the starting of the motor alcohol or the usual alcohol-benzol mixture. It is necessary in this case to start the motor with benzine before using the alcohol, which makes two containers and two carburettors necessary.

Canada produced in the calendar year 1916, 7·5 million gallons of crude petroleum valued at $392,300. The imports of crude and refined petroleum were about 290 million gallons valued at about $14,000,000. It can be seen that Canada is dependent on foreign sources for her supplies of petroleum and petroleum products. In 1916 the imports of refined and illuminating oils amounted to over 8,000,000 gallons valued at $540,000 and during the same year 18,000,000 gallons of gasoline were imported. If industrial alcohol could be produced economically in Canada it would mean a saving in imports of over $4,000,000.

On the basis of a manufacturing cost of $0.185 to $0.32 per Imperial gallon for 100 per cent alcohol from waste sulphite liquor there ought to be some hope, if suitable markets and legislation were provided, to introduce this alcohol for industrial purposes. The total production of alcohol from waste sulphite liquor would be about 3,320,000 gallons of absolute alcohol, which would assist in freeing Canada from dependence on foreign sources as well as utilize a waste product.

The manufacture of alcohol from waste sulphite liquor does not solve the waste liquor problem completely as only about 15-20 per cent of the total solid of the liquor is utilized. But the residual liquor from the alcohol process may be made useful by employing one of the other processes, for instance in producing binding material, fuel, or using the dry substances for destructive distillation.

The use of waste sulphite liquor products for cattle food has not given very satisfactory results, and as a fertilizer the waste liquor has only an indirect value, as it contains the chief chemicals required of a good fertilizer, namely nitrogen and phosphate, in very small quantity. It may, however, be useful in mixture with other products such as cyanamide, and may improve a soil poor in humus on account of its organic substances which form a good medium for the growth of nitrogen-fixing bacteria.

As a mordant the sulphite lignin or more correctly the substances precipitated by albumin or gelatin or salted out with sulphate or chloride of sodium, have been proposed under names such as lignosin and lignorosin. Of theoretical interest, but still without any practical value, are the condensation products with aromatic amines and the preparation of azo-dyes by coupling aromatic di-azo compounds with lignin sulphonic acid or its salts, obtained from waste sulphite liquor.

Recently it was suggested that sulphur dyestuffs might be prepared by heating sulphonic acids or sulphonates with alkali sulphides or other sulphur-containing substances, dissolving the product in water and precipitating with acid, but all the attempts in producing dyestuffs from the waste sulphite liquor are still limited to laboratory experiments.

The precipitation of organic substances at high temperature and pressure as suggested by Strehlenert, for use as a fuel or for destructive distillation, is probably, in the present form, not of immediate interest to Canada, but the development of this very interesting process should be followed with the greatest interest by the sulphite pulp manufacturers. It is evident from the facts collected in this publication that only very few of the proposed processes have reached any industrial importance and that there is an immense field open for scientific investigation and practical application before the problem is solved.

A research laboratory has recently been established in Sweden for the purpose of investigating the waste sulphite liquor problem. This laboratory will carry on research on the more important problems connected with the utilization of the waste liquor and will endeavour to work out new methods for its utilization.

COMPOSITION

Considering the importance of an exact knowledge of the raw materials used in any chemical process, it is surprising that the great sulphite industry reached such a point of perfection before the nature of the chief raw material, the wood, had been thoroughly investigated. The development of special methods for wood analysis in the last few years has allowed a more intimate study of the constitution of the woods, and much important information has been secured regarding the characteristics of various species. However, our knowledge of the exact composition of the woods used in the sulphite pulp industry and, therefore, of the details of the cooking process is still too limited to permit of any definite conclusions with regard to the apparently very complicated composition of the waste sulphite liquor. On the other hand considerable work has been done by the most able investigators to determine the nature of the substances present in the waste liquor. The results of these investigations, which date back to the early years of this industry, not only furnish a valuable material for a better understanding of the cooking process as well as of the chemical characteristics of the wood but they are also of the greatest importance in the discussion of the value of certain processes for utilization of the waste sulphite liquor.

The chief constituents of European spruce wood are according to Klason:—

Cellulose	about	50	per cent
Carbohydrates	"	16	"
Lignin	"	30	"
Protein		0·7	"
Rosin and fat		3·3	"

These figures no doubt give an excellent idea of the nature of the average wood material employed in European mills. But there is less uniformity in this raw material on the American Continent, due to the employment of different species such as black, red, and white spruce, balsam fir, hemlock, etc. which vary considerably with regard to their chemical composition.

The following table contains average values for the ordinary Canadian pulp woods:—

—	Cellulose.	Lignin.	Resin.	Pentosan.
	%	%	%	%
White spruce	55	26	1·0	11
Black spruce	55	26	0 75	11
Balsam fir	51	29	1·50	11
Hemlock	49	26	1·75	12

The cellulose is determined by treating the wood, after removal of resins, with acetic acid in glycerin followed by the usual chlorination method, as suggested by Cross and Bevan. This cellulose is not absolutely identical with cotton cellulose, as it still gives the furfural reaction due to the presence of substances which are apparently so intimately attached to the cellulose that they can not be removed without partly destroying the cellulose itself and are not removed even at the high temperature and pressure prevailing in the sulphite digester. In fact it has been found that the amount of furfural-yielding substances in the cellulose residue after chlorination treatment corresponds to that of a high-grade sulphite pulp, about 70 per cent of the total of these substances present in the wood being removed in the cooking process as well as by this method of cellulose determinations. As the other impurities, chiefly lignin in both cases, can be completely dissolved out, the figures given for cellulose may be regarded as correct values for pulp obtainable. The lignin is determined by dissolving out all the other substances with 72 per cent sulphuric acid after the resins have been removed. The values for pentosans are calculated from the yield of furfural from the original wood, making allowance for those substances still remaining in the cellulose residue which gives the furfural reaction. This of course is not absolutely correct, as part of the furfural may be traced back to other substances such as pentoses, furfuroids, etc., but there is no reason to believe that there is much variation in these substances in the different species as the furfural yield is practically the same in all these woods. Assuming Klason's value of 0·7 per cent protein for these woods we obtain a good idea of their chief constituents. It must be remembered that the values given in the table are by no means absolute for all trees of the same species. It has been found that the cellulose content varies in the same tree with the distance from the ground and that in white spruce two samples taken at a distance of 48 feet apart show a difference in cellulose of as much as 4 per cent. There are also slight variations in the resin content of different parts of the same tree. The lignin content seems to increase with the distance from the ground, but not in proportion to the decrease in cellulose. The remainder of non-cellulose substances in the wood represents chiefly lower carbohydrates which are easily hydrolyzed and can be partially dissolved out with boiling water. The nature of these substances has not been sufficiently studied although they are apparently of great importance, furnishing as it seems the chief raw material for the fermentable sugar in the waste liquor. Schorger (J. Ind. Eng. Chem., vol. 9 (1917), p. 554) found that the coniferous woods contain appreciable quantities of mannan and discovered in one white spruce as much as 7 per cent of this sugar. Klason, however, found only 2·5 per cent mannose but 7·9 per cent glucose and 1·3 per cent galactose. It was mentioned above that high-grade sulphite pulps contain very little or no lignin, that, further, a large proportion of the furfural-yielding substances and other lower carbohydrates are removed by hydrolysis in the cooking process. The resins and fats are only incompletely removed. It is therefore possible by means of these analytical data to form an opinion regarding the substances that may be expected in the waste liquor, but the quantity of these substances will naturally depend on many factors such as the species, the size of the wood, and cooking conditions such as condensation, relieving, temperature, and pressure. The quantity of fermentable sugar especially may depend largely on the last two factors, and must evidently be regarded as the residue of sugar present in the wood or formed at an early stage of the cooking process. Great differences would therefore be expected in liquors from Ritter-Kellner cooks as compared with those obtained by the Mitscherlich process, due to the higher pressure and temperature in the former. The variations in method of cooking by the Ritter-Kellner process may also account for the variations in the results arrived at by different investigators. Another point which seems to be of importance is that the liquor may change a good deal when left standing for a considerable period. As the liquors in most cases must be used immediately after the end of the cook the analysis of the fresh waste liquor will be of most interest.

During the process of cooking, liquor as well as gas is relieved from time to time. In this way large quantities of sulphurous acid escape and are recovered by special apparatus and returned to the acid system. Besides sulphurous acid the vapours also contain other volatile products, which can be condensed in special apparatus and purified. Bergstrom found that the condensate thus obtained at a certain period of the cook, amounting to 400-600 litres per ton of pulp (79-120 gallons per short ton), contains, besides about 100 grammes (0·22 pound) of sulphurous acid, 5-5·5 grammes of methyl alcohol per litre, which is equivalent to about 2·6 kilogrammes per ton of pulp or 5·2 pounds per short ton. The oil which floats on the top of the condensate is a complex mixture consisting largely of cymene and containing a small quantity of furfural and a solid terpene alcohol.

The crude alcohol obtained from the condensate contains acetone, acetaldehyde, and other substances such as traces of acetic and formic acids, but the alcohol can easily be purified. From the oils cymol can readily be produced in a pure state and furfural may be obtained in small quantities and purified.

Only about one-third of the total methyl alcohol formed in the cooking process is present in the condensed vapours. The quantity of methyl alcohol as well as of the other substances depends mainly upon the method of relieving and the temperature and pressure, at the time of blowing. Therefore, most of these volatile substances can be found in the waste liquor in greater or less amounts, depending upon the method of cooking. For example it has been found that the furfural content of the Ritter-Kellner liquor is considerably higher than in the Mitscherlich liquor; in fact the difference is so great that it may serve as a qualitative reaction for the identification of these liquors.

The waste liquor, which has a specific gravity of about 1·05 and gives an acid reaction, contains about 12 per cent organic and 1-1·5 per cent inorganic substances. The dry residue, in other words, contains 10-15 per cent of ash. Of the 6-10 per cent of sulphur present in the liquor only 2 per cent remains in the ash mainly as $CaSO_4$ and CaS, as most of it escapes as SO_2 when the liquor is heated. There is always a small quantity of sulphurous acid in the liquor in the free form and loosely combined with sugar, so that it may be removed to a large extent by heating with or without the addition of an acid. Besides sulphurous acid the liquor also contains small quantities of sulphuric acid, acetic and formic acids, oxalic acid, and traces of citric acid. Among the other substances detected in small quantities in the waste sulphite liquor, according to Tollens and Lindsey, are vanillin, identified by the odour test, and succinic and protocatechuic acid identified by their decomposition products, pyrrole and pyrocatechin. In the rectification of alcohol from the waste liquor a reddish-brown oil separates out from which Klason and Segerfelt recovered optically inactive borneol similar to that obtained by treating turpentine with sulphuric acid. The borneol may be formed in the digestion process from bornyl acetate (or a similar ester) originally present in the volatile oils of the wood.

Cross and Bevan discovered that when glue is added to the waste liquor a precipitate is obtained which is soluble in alkali or sulphites and which may serve as a substitute for rosin size, since the solution may be precipitated by aluminium sulphate. This behaviour towards animal glue has been regarded as a reaction of tannin compounds, but it is claimed by the tannin industry that if tannin is present at all it must be in a very small quantity.

The carbohydrates and the lignin are the sources of the most important constituents of the waste liquor, namely, the sugars and the calcium salt of the lignosulphonic acid.

The liquor gives the reaction of carbohydrates, reduces Fehlings solution strongly and also dyestuffs and chromium salts. Further, it gives an osazone precipitate with phenyl hydrazine and yields furfural on distillation with hydrochloric acid. Krause, who studied the sugars in the liquor from a Mitscherlich cook (indirect cooking) and from a Ritter-Kellner cook (direct cooking), obtained the following results:—

—	Ritter-Kellner.	Mitscherlich.
	%	%
Total sugars	1·47	1·48
Pentoses	0·41	0·47
Mannose	0·48	0·48
Galactose	0·01	0 01
Fructose	0·25	0·28
Dextrose	trace	....

More recently Klason has published some results of his investigations of the sugars present in a Ritter-Kellner liquor which differ considerably from those arrived at by Krause, as is shown in the following table:—

Mannose	0·526 per cent
Galactose	0·279 "
Glucose	1·65 "
Arabinose	0·90 "

Although the fermentable sugars represent only a very small percentage of the organic substances in the waste liquor they form the raw material for the most promising processes for its utilization at the present time, namely the production of alcohol. By far the greater proportion of the solid matter in the liquor is present as a lignin-calcium compound, the lignin substance of the wood combining with the sulphurous acid during the cooking process to form sulphonic acids. The calcium compound of these sulphonic acids may be precipitated from the concentrated liquor by alcohol, or by sodium chloride or magnesium sulphate. Concentrated mineral acids and lead acetate also precipitate the salt. The purification of the salt, however, is very difficult as it does not crystallize from its solutions. The compounds obtained by precipitation have been analysed by various investigators, and formulæ for the salt and for lignin sulphonic acid, as well as for lignin, have been deduced from the results obtained. The most important investigations on this subject have been carried out by Klason, and the interesting results of these investigations will be found in the literature, especially his book "Beitrage Zur Kenntniss der Chemischen Zusammensetzung der Fichtenholzes" ("Contribution to the Knowledge of the Chemical Composition of Spruce Wood".) Klason succeeded in separating in a high state of purity the barium salt of the lignin sulphonic acid in the following manner: The liquor was concentrated in vacuo till nearly dry and the residue dissolved, by which means part of the gypsum and sulphite were separated out. The liquor was then neutralized with calcium carbonate and crystallized calcium chloride was added as long as it went into solution, in which manner a thick precipitate was formed. The liquor and precipitate were then boiled for 3 hours, after which the precipitate was separated out and washed with alcohol. In this way only about one-half of the calcium salts of the liquor was obtained. In order to transform this salt into a barium salt, sulphuric acid was added in a quantity corresponding to the amount of lime present. The liquor was then concentrated at ordinary temperature to a thick consistency, whereupon alcohol was added. The gypsum was separated out and the alcohol evaporated off at ordinary temperature. The liquid was then diluted with water and neutralized with barium hydrate, the amount required having been previously determined by titration. As it is usually difficult to filter the liquid, alcohol was carefully added until a precipitate was just formed. Before the addition of alcohol the liquor was allowed to stand till all barium sulphate formed had settled. The barium ligno-sulphonate was precipitated from the clear solution by the addition of alcohol. According to Klason the analysis of this salt points to the formula $C_{40}H_{44}O_{17}S_2Ba$, and accordingly the lignin must have the composition $C_{40}H_{42}O_{11}$ or, as the molecular weight of the barium salt has been found to be at least 6,000, the formula may be $(C_{40}H_{42}O_{11})_6$. It has been mentioned above that only about one-half of the lignin-calcium compound is precipitated from the waste liquor. From the high methoxy content of the precipitate and that of the wood, Klason concludes that there is a second lignin in admixture with the first, with no, or at least a very low methoxy content and a higher hydroxyl content, and has suggested the formula $C_{38}H_{38}O_{12}$ $(C_{40}H_{42}O_{11}\text{-}2CH_2+O)$; the lignin represents chiefly a condensation product of coniferyl alcohol and hydroxy coniferyl alcohol, the groups apparently having the same position as in gallic acid, namely, 1, 3, 4, and 5.

In the formation of the sulphonic-acid salt in the cooking process it is stated that two molecules of SO_2 are added to the lignin, forming a sulphonic acid. Besides this the lignin can combine with two more SO_2 molecules one of which is very loosely attached so that it may be partially titrated with iodine at ordinary temperature, whereas the second molecule is more closely combined but can be separated quantitatively by evaporation and the addition of barium chloride to the liquor. Klason therefore assumes that the lignin complex has three ethylene bounds,two of which bring about the intimate addition of two SO_2 molecules forming lignin sulphonic acid, the third group binding SO_2 more loosely. The fourth SO_2 molecule is attached to an active carbonyl (aldehyde or ketone group) so loosely that the sulphurous acid can be separated from it at ordinary temperature. The formula for lignin which Klason has proposed is meant to represent a summary of facts concerning the reactions of the lignin compound, and must be confirmed by future exact analytical investigations. It has, however, as Schwalbe remarks, "an advantage which should not be undervalued, namely that Klason's speculations give a splendid working hypothesis for the sulphite cooking process, for which it is really intended."

Wichelhaus has given the following table of the quantitative composition of a waste sulphite liquor:—

Dry residue	82·8350	grammes in one litre
a) organic	68·3440	" "
b) inorganic	14·4910	" "
H_2SO_4	3·4340	" "
SO_2 combined	5·8420	" "
SO_2 free	2·5600	" "
Cl	0·0240	" "
SiO_2	0·0024	" "
Fe_2O_3 and Al_2O_3	0·0102	" "
CaO	7·1760	" "
MgO	0·0040	" "
Alkalies	0·0192	" "
Specific gravity	1·0390	" "
Reaction	Acid	" "

Concerning the nature of the organic substances Klason has given the following summary of the waste products calculated on one metric ton of pulp:—

——	Liquor I.	Liquor II.	Liquor I.	Liquor II.
	Kilogrammes.	Kilogrammes.	Pounds per Short Ton.	Pounds per Short Ton.
Lignin	644	600	1,287	1,200
Carbohydrates	311	325	622	650
Proteins	15·5	15	31	30
Rosin and fat	73	30	146	60
Sulphurous acid combined with the lignin	235	200	470	400
Lime	102	90	204	280
	1,380	1,260	2,760	2,520

Frank, A.—THE CHEMICAL PROCESS IN SULPHITE COOKING.

The sugar value of the waste liquor, the difficulties in fermentation, and the unpleasant odour of the sulphite spirit are discussed.

Papier-Ztg. vol. 14 (1889) p. 1556.

Barth, K.—SULPHITE LIQUOR.

The author found that the separation of $CaSO_3$ takes place at the moment when the liquor has the composition $CaH(SO_3)_2$. The oxidation of H_2SO_3 to H_2SO_4 or $CaSO_3$ to $CaSO_4$ does not take place without the presence of wood or increased pressure.

Papier-Ztg. vol. 15 (1890) p. 667.

Buddens, W.—ORGANIC ACIDS OF SULPHITE LIQUOR.

Gives proof of existence of succinic and protocatechuic acid in sulphite liquor. The digallic acid (tannin) originally present is probably changed by the SO_2 into diprotocatechuic acid, which has tanning properties.

Papier-Ztg. vol. 16 (1891) p. 1813.

Harpf, A.—CHEMISTRY OF SULPHITE PROCESS.

During the cooking process the H_2SO_3 is oxidized to H_2SO_4 but forms a water-soluble calcium salt of a sulphur containing organic acid.

Dingler's polytech J. (1892).
Hofmann. Handbuch der Papierfabrikation 2nd edition (1897), pp. 1546, 1623.
Papier-Ztg. vol. 16 (1891) pp. 1726, 1844, 1908, 1964, 2155, and vol. 17 (1892) pp. 1089, 1121.

Weld, F. W., Lindsey, J. B., Schnelle, W., and Tollens, B.—ON THE SO-CALLED "SULPHITE-LYE" AND ON THE ROTATION OF GLUCONIC, GALACTONIC, AND RHAMNONIC ACIDS.

Mannose and galactose are found in the liquor, which yields furfural on distillation with HCl, proving that pentaglucoses or pentoses are also present. The presence of saccharic acid could not be proved, but vanillin was found by means of the phloroglucinol reaction. A table shows that the acids obtained by oxidation from glucoses possess a remarkable kind of bi-rotation.

Ber. vol. 23 (1890) p. 2990.
J. Soc. Chem. Ind. vol. 10 (1891) p. 156.

Lindsey, J. B. and Tollens, B.—SULPHITE LIQUOR AND LIGNIN.

The soluble by-products of the bisulphite process of pulping wood are derivatives of its lignin or lignone constituents, and the authors have investigated these waste liquors with the view of elucidating the constituents of the latter. The results of a general examination for carbohydrate constituents showed (1) the absence of dextrose or bodies yielding dextrose, (2) the presence of galactose, mannose, pentaglucose or derivatives of these. A series of observations of yeast fermentations of the liquor, after expelling sulphurous acid by evaporation with sulphuric acid, showed the formation of 5-6 c.c. alcohol from 1 litre of the wood liquor, (containing 95 grammes total solids). After hydrolysis by boiling with acid, the quantity of alcohol formed amounted to 6.75 c.c. It is obvious that these by-products are for the most part insusceptible of alcoholic fermentation.

The greater proportion of the constituents of these sulphite liquors are precipitated by lead acetate. This precipitate decomposed by sulphuric acid gave a solution from which alcohol threw down a flocculent substance having the empirical composition $C_{26}H_{30}SO_{12}$; the filtrate from this on evaporation yielded a gummy body, analysis of which also gave numbers expressed by the formula $C_{26}H_{30}SO_{12}$. The addition of hydrochloric acid to the original liquor precipitated a body $C_{26}H_{30}SO_{10}$; and bromine threw down a brominated derivative $C_{26}H_{28}Br_4SO_{11}$.

These products boiled with hydriodic acid for the determination of OCH_3 gave numbers proving the presence of 2 CH_3 groups in the above empirical formulae. The S is present as SO_3H. For the original constituents of the pine wood, of which these bodies are sulphonated derivatives, the authors arrive, after discussion, at the formula $C_{24}H_{24}(CH_3)2O_{10}$ and point out its substantial identity with that assigned by Dietrich and Konig (Landw. Vers. Stat. vol. 13, p. 222) to the lignin of woody tissue, as with that taken by Cross and Bevan for the lignone constituent of jute (Chem. Soc. J. vol. 55, p. 213).

Ann. vol. 267 (1892) p. 341.
Ber. (1893) p. 322.
J. Soc. Chem. Ind. vol. 11 (1892) p. 835.

Lindsey, J. B. and Tollens, B.—SULPHITE LIQUOR AND LIGNIN.

" The liquor experimented with was prepared by the Ritter-Kellner process. It was yellow and almost clear, and when fresh smelt slightly of sulphurous acid, the quantity of which was increased by heating with dilute sulphuric acid. It had a specific gravity of 1.055, decolorized iodine solution, and strongly reduced Fehling's solution on warming—a result not to be ascribed to the sulphurous acid present as this has no such action in alkaline solution. Phenyl-hydrazine acetate gave a fairly copious yellow turbidity which became darker on standing and finally separated as a dark, tarry mass. A precipitate of barium sulphate was produced on adding barium chloride to the wood-pulp solution after the addition of hydrochloric acid; lead acetate gave a dense yellow precipitate, leaving the filtrate clear and colourless. A solution of gelatin gave a grey precipitate which cohered in clots on stirring.

"Seeing that, according to Wehmer and Tollens, the formation of levulinic acid on heating organic substances with hydrochloric acid is a certain indication of the presence of hexacarbohydrates, the fact that only a small quantity of the silver salt could be obtained from sulphite liquor goes to show that lignin does not fall into this class of bodies. A trace, at most, of dextrose was found by the saccharic acid reaction of Gans and Tollens. The presence of a small quantity of galactose or galactan was recognized by the formation of mucic acid. Mannose was detected by the formation of its hydrazone which melted at 187° C. and was further identified by its ultimate analysis and behaviour on polarisation. The quantity obtained was 3·4 grammes of the hydrazone from 500 c.c. of the liquor, which was increased to 5 grammes when inversion had been previously performed. Pentoses were recognized by means of the furfural reaction, furfuramid melting at 114° C. being ultimately obtained. On evaporating liquor to a syrup, adding alcohol, and boiling, a considerable amount of gummy matter separated out. After this had been freed from residual gummy matter the final alcoholic extract had an odour of vanillin and gave the phloroglucin reaction for vanillin; the presence of xylose was negatived by the spectroscopic examination of the alcoholic solution of the phloroglucin precipitate. It therefore appears certain that vanilla, or some closely analogous body, must be present in sulphite liquor, although it has not been isolated in the crystalline state.

" An experiment was made to ascertain the capability of the liquor of fermenting. The sulphite was decomposed by a slight excess of sulphuric acid and fermentation effected by fresh yeast with the addition of a small amount of a nutritive material derived from the same yeast. From 1 litre of the liquid thus treated 0·0456 per cent of alcohol by volume was obtained. Therefore, out of a total amount of solid matter of 9·46 per cent not more than about 1·2 per cent consists of fermentable carbohydrates.

"The cause of the yellow precipitate with lead acetate was investigated. A portion of the fluid from which sulphuric acid had been eliminated by means of baryta water was precipitated with lead acetate, and the precipitate analysed. It had a composition of which the organic portion was expressed by the formula $C_{26}H_{30}O_{12}$ or $C_{26}H_{32}O_{12}$.

" The crude lead precipitate was decomposed with sulphuric acid, and the excess of acid removed by digestion with a second portion of the precipitate, and the resulting solution, which gave no reaction with phloroglucin, was concentrated and diluted with alcohol. A grey flocculent precipitate, which, after purification by means of alcohol and ether and drying over sulphuric acid, gave results corresponding to the formula $C_{26}H_{30}SO_{12}$ or $C_{24}H_{24}(CH_3)_2SO_{12}$. The filtrate from this grey body yielded on evaporation to dryness a substance of the formula,—

$$C_{24}H_{24}\,(CH_3)_2\,SO_{12} + 1\tfrac{1}{2}\,H_2O$$

which reduced Fehling's solution. A substance was also precipitated from the original sulphite liquor by hydrochloric acid, to which was assigned the formula $C_{26}H_{30}SO_{10}$, and a brominated derivative was also obtained $C_{26}H_{28}Br_4SO_{10}$. The authors deduce from these observations that the gummy material from which the above sulphur-containing bodies are formed has the composition $C_{24}H_{24}(CH_3)_2O_{12}$, or $C_{24}H_{26}(CH_3)_2O_{12}$, assuming that the sulphur is not in direct union with the oxygen. Should the contrary be true, and the sulphur be present as a sulphonic group, the above formula would be reduced by two or three atoms of oxygen. According to Mitscherlich, sulphite liquor contains tannin, a supposition upheld by its behaviour with gelatin, hide powder, and lead acetate, but opposed to this is the absence of reaction with iron salts and the divergence in composition noted above. Nevertheless, if it be assumed that the sulphur is present as a sulphonic group, in the substance capable of precipitating gelatin a resemblance to the bodies prepared from sundry phenols by Schiff, which he termed, 'sulphurized tannins,' becomes apparent, as they also fail to give the iron reaction."

Thesis. Göttingen (1891).
Z. angew. Chem. vol. 5 (1892) p. 154.
J. Soc. Chem. Ind. vol. 12 (1893) p. 287.

Ahrens, F. B.—SULPHITE LIQUOR OF CELLULOSE PULP MILLS.

The author, in conjunction with E. Klingenstein, had occasion to examine waste liquor at the Agricultural Technological Institute of the University of Breslau, the following being the results: Sulphite waste liquor is a reddish-brown, cloudy liquor, with strong acid reaction, a peculiar smell, a specific gravity of 1·0465 (6·5° Bé.) at 15·8° C. When evaporated a tough, sticky, gummy substance remains ("solid matter") amounting to 9·4 per cent, of which 1·11 per cent is ash and 8·29 per cent organic matter. A slight error occurs in all the results herein recorded, which the authors point out. It is due to the fact that the "ash" consists of sulphate and sulphite of lime, which in calcining is partly reduced to calcium sulphide and thence to sulphuretted hydrogen, which burns off as SO_2. This slight loss was thus credited as "organic matter."

PURIFYING THE LIQUOR WITH LIME

The liquor as it leaves the boilers is strongly acid, containing a considerable quantity of recoverable sulphurous acid which may be obtained as sulphite of lime by the addition of sufficient lime to nearly neutralize the solution. To complete the neutralization the liquor may be run over limestone. A precipitate obtained by the addition of lime contains a certain quantity of organic matter, varying according to the temperature and the amount of lime added.

I. RESULTS OF EXPERIMENTS

The hot liquor was treated with a measured quantity of fresh milk of lime, boiled and filtered, the filtrate being then neutralized by carbonic acid.

Number.	CaO.	Solid Matter.	Ash.	Organic Sub.
	%	%	%	%
1	2	8·75	1·80	6·95
2	3	7·48	1·59	5·89
3	4	7·36	1·71	5·65
5	6	8·86	1·52	5·34
7	8	6·65	1·54	5·11
9	10	6·79	1·51	5·28 x
11	12	6·52	1·49	5·03 x
12	15	6·31	1·49	4·82
13	20	7·00	1·60	5·40
14	30	4·99	1·01	3·98

By a further addition of lime the organic matter precipitated increases, and by longer boiling with lime the organic compounds are again brought into solution, which fact explains the results marked X in the above table.

II. RESULTS OF EXPERIMENTS

Measured quantities of fresh milk of lime were added to the liquor when cold, the precipitate filtered off, and the filtrate neutralized with CO_2 and examined, the results being:—

Number.	CaO	Solid Matter.	Ash.	Organic Sub.
	%	%	%	%
1	2	6·21	1·11	5·10
2	3	6·19	1·33	4·96
3	4	5·26	1·00	4·26
4	6	5·08	1·04	4·04
5	8	4·96	1·10	3·86
6	10	5·67	1·22	4·45
7	12	5·76	1·23	4·53
8	14	6·26	1·29	4·97

It is seen that the minimum of organic substance is left in the liquor (3·86 per cent) by treating with 8 per cent of lime, a regular increase taking place with an increase in the lime used. Upon adding the lime the liquor turns from yellow to red and brown.

Treatment of the liquor with alumina. A number of tests were made to ascertain the quantity of organic matter that could be mechanically carried down, by means of gelatinous alumina prepared by decomposing aluminate of soda with CO_2. The liquor was treated with known quantities of aluminate of soda and then saturated with CO_2 at the ordinary temperature. Results:—

Number.	Al_2O_3.	Solid Matter.	Ash.	Organic Sub.
	%	%	%	%
1	1	9·58	2·06	7·53
2	2	9·22	2·18	7·04
		9·38	2·11	7·27
3	4	8·53	2·13	6·40
4	5	8·2	3·10	5·10
5	6	10·84	3·96	6·88

DRY DISTILLATION OF THE RESIDUE

As already pointed out the residue obtained by simply evaporating the liquor to dryness is a dark, gummy, tough substance, whereas the residue obtained after treatment with lime is a firm, friable material. The ash and total sulphur contained in this were estimated. Ten litres of liquor were boiled with 138 grammes of CaO and filtered; the residue amounted to 835 grammes and gave by analysis the following: 22.37 per cent of ash and 6.45 per cent of total sulphur; of the ash, 14.4 per cent consisted of sulphur of which 13·4 per cent existed as SO_3 and 58·5 per cent as CaO. By the dry distillation of this residue a considerable quantity of gas was evolved, mostly H_2S, the formation of which is probably due to the reduction of the sulphites and sulphates by the organic matter. The distillate is a liquid of penetrating odour from which sulphur separated on standing, and the residue consists of a black pitch. The distillate was acid and contained acetic acid, acetone, mercaptan, and an oil containing sulphur with an unpleasant smell. The two latter are produced by the secondary reaction between the H_2S and the methyl alcohol, and a smaller number of nitrogeneous bases. The pitch contained 33·6 per cent of ash and 4·37 per cent of total sulphur; the ash contained 71·6 per cent of CaO and 13·7 per cent S, of which 12·5 per cent existed as SO_3. Similar results were obtained by the dry distillation of the lime precipitate.

BY OSMOSIS

The following diffusion tests were conducted in the ordinary way. In the cell there were 10 litres of liquor and 10 litres of water. At first a test was taken every hour, but this was found to be unnecessary. The surrounding water increased in colour and became somewhat acid, and had no action on polarised light. P. Schubert obtained the following results:—

Days.	Solid Matter.	Ash.	Organic Matter.
	%	%	%
1	1·95	0·33	1·62
2	2·46	0·49	1·97
3	2·98	0·52	2·46
5	3·95	0·63	3·32
7	4·10	0·67	3·43
10	4·44	0·71	3·71

The diffused liquor after 10 days had a specific gravity of 1.020.

ELECTROLYTIC EXPERIMENTS

In one of these experiments a liquor was employed that had been treated with lime and neutralized with CO_2, lead plates being the electrodes. After about two hours action of a current from three large Bunsen elements, a slimy precipitate separated, the liquor turning a light yellow colour, and the lead was dissolved to considerable quantities. A quantitative test gave the later mentioned results. By electrolysis a liquor was obtained which was treated cold with 3 per cent of lime and by neutralizing with CO_2 became somewhat heated. It was of a dark red or brown colour and contained 6.9 per cent of dry substances, 1.33 per cent of ash, and 4.86 per cent of organic matter. The lead plates had 159 cm. of acting surface and were separated 0.3 cm. from each other. The current was 5 amperes. The length of time during which the current passed was 110 minutes. After separating the lead by sulphuretted hydrogen, and calculating upon the original volume, there were found 4.42 per cent dry substance, 1.07 per cent ash, and 3.35 per cent organic matter. The experiment showed without a doubt a great diminution of organic substance. Another trial was made with a platinum electrode, the size of the plates, the strength of current, etc., being as before. The liquor employed, which had been treated with 5 per cent of lime whilst hot, was neutralized with CO_2 and contained 7.13 per cent of dry substance, of which 1.56 per cent was ash and 5.57 organic compounds. The experiment lasted two hours. Only a small precipitate was produced but the liquor became nearly black. By analysis 6.3 per cent of dry substance was obtained, of which 1.5 per cent consisted of ash and 4.85 per cent of organic matter. The above experiments clearly indicate that with lead electrodes the purifying effect is partly due to the lead; the electric current also has the effect of reducing the organic matter. It appeared desirable to ascertain the effect of a stronger and a higher tension current. By means of a dynamo a current was employed of 70 volts and 10 amperes, and of 106 volts and 19 amperes. As electrodes, lead and zinc plates were used. The liquor employed was treated with 3 per cent of lime whilst cold, was filtered and neutralized with CO_2, and showed by analysis 4·96 per cent organic substance. The precipitate formed was very small and the liquor became strongly heated. The analysis in the one case showed 6·5 per cent of dry substance, 0·23 lead, 1·27 ash, and 5·0 organic compound, and in the other 6·51 of dry substance, 0·15 zinc, 1·48 ash, and 4·98 organic compound. No further effects were produced by the use of currents of higher tension. It is a well known fact that in the manufacturing of sulphite wood-pulp a boiling operation occasionally requires a much longer time than usual, and the reason being unknown a number of experiments were conducted as follows: the liquor was treated with 3 per cent of lime, and the precipitate was pressed and stirred in water. Into the solution SO_2 was then passed until it smelt strongly of the latter. For several hours it was heated from 125° to 130°. In every case considerable quantities of sulphuric acid compounds were obtained, the quantities varying according to the degree of saturation with SO_2 and the heating. From 100 grammes of dry precipitate the minimum increase of H_2SO_4 was 2.6 grammes and the maximum 5.9 grammes.

Z. angew. Chem. vol. 8 (1895) p. 41.
J. Soc. Chem. Ind. vol. 14 (1895) p. 503.

Ulzer, F. and Seidel, H.—SULPHITE CELLULOSE WASTE LIQUOR.

Of the dry residue 5.97 per cent and of the liquor 0.807 per cent are sulphur. The part in the form of organic compounds amounts to 0.60 per cent. The high content of carbohydrate-like substances which can be salted out is very striking. The different proposals for use of liquor are considered. Graf Andrassay's proposal for evaporation of liquor in open pans, by furnace gases on counter current principle. Coal briquetting.

Mitt. Techn. Gew. Mus. vol 6 (1896) p. 186.

Knoesel, Th.—WASTE SULPHITE LIQUORS.

Papier-Ztg. vol. 23 (1898) part I p. 1503.

Hofmann, C.—PRAKT. HANDBUCH DER PAPIERFABRIKATION.

Berlin 1875, 2nd Edition vol 1 (1891) vol. 2 (1897) p. 1575-1628.

Harpf, A.—UTILIZATION OF WASTE SULPHITE LIQUOR.

Report on papers read before the Third International Congress for Applied Chemistry in Vienna, 1898.

Z. angew. Chem. vol. 11 (1898) pp. 875, 925, 1169.

Seidel, H.—WASTE LIQUORS FROM "SULPHITE" WOOD PROCESS.

The liquor investigated by the author was obtained from a Silesian mill working the Ritter-Kellner process.

The following analytical results may be noted: specific gravity 1·050; total solid residue (dry at 100°) 12.013 grammes per 100 c.c., i.e. 11.44 per cent, containing 9.54 per cent total sulphur. The data concerning sulphur are as follows, calculated in this case as per cent of the liquor:—

Sulphur in dry residue, per cent of liquor	1·0910
Sulphur as free SO_2	0·0320
Sulphur as SO_3	0·0074

of the total sulphur of the liquor, 93 per cent exists in the form of "organic" compounds.

In reference to the claim of the value of these liquors as fertilizers, by reason of their potassium salt contents, a determination of potash was made and found to amount to 1 gramme of K_2O per 52 litres.

A study of the precipitates obtained by various processes of "salting-out" e.g. Ekman's series of so-called "Dextron" products (German Patent 81,553), confirms the author's previous conclusion that this method of fractionation of the organic constituents of the liquor fails to bring out any constitutional differences. A similar conclusion results from a study of the fractions obtained by precipitation with alcohol. The analysis of a carefully purified fraction gave the following numbers: C, 56.27 per cent; H, 5.87 per cent; S, 5.52 per cent in closest agreement with numbers obtained by Lindsey and Tollens, and corresponding with the empirical formula $C_{26}H_{30}SO_{12}$. It is noted also that the results of these chemists were obtained with a liquor from a mill working under the different conditions of the Mitscherlich process.

Respecting the theory of the reactions taking place in the digesters, the author advances no new hypotheses, but generally confirms those summarized in "Cellulose" (Cross and Bevan), pp. 177 to 201.

Mitt. Techn. Gew. Mus. vol. 7 (1897) p. 119.
J. Soc. Chem. Ind. vol. 17 (1898) p. 178.

Seidel, H. and Hanak, L.—WASTE SULPHITE LIQUOR.

In previous articles the authors have shown that an organic substance containing sulphur can be obtained from waste sulphite liquor in different ways, and the products were proved to be similar by the corresponding amount of sulphur contained therein.

Since then, different boilings from the same Silesian cellulose-mills have been analysed and the former statements corroborated.

The products obtained reduce Fehling's solution, are soluble in water, are insoluble in absolute alcohol, and in the concentrated solution of common salt give a precipitate with phenyl-hydrazine, give the reaction with a-naphthol and H_2SO_4, give the same shades of colour with $FeCl_3$ and almost the same percentage of mineral ash, and sulphur. They also give precipitates with barium chloride and lead acetate, soluble with difficulty, but cannot be completely precipitated by the latter reagents.

The percentage of sulphur was slightly lower than in the products first analysed, being about 8 per cent, but it always corresponded within narrow limits in the products of the same liquor, again showing the identity of the organic products and also proving that the amount of organically-combined sulphur depends upon the manner of conducting the boiling process.

To obtain the principal constituents of the organic matter as pure as possible a dilute solution of waste liquor was acidified with HCl and boiled, and to this barium chloride was added in the quantity calculated to completely precipitate the sulphuric acid present. The filtrate showed no turbidity with either barium chloride or sulphuric acid, and as the barium salt of the organic substance is soluble in water this filtrate therefore contained it in solution. After evaporating part of the latter, alcohol was added and a precipitate obtained which the authors termed "Gum free from sulphuric acid." This precipitate yields 13·32 per cent of ash, which calculated as calcium sulphates, gives the percentage of CaO as 5·64. With oxalic acid the CaO was calculated as 5·66 per cent. The amount of sulphur contained was 8·44 per cent. The substances show all the before-mentioned reactions.

The authors then endeavoured to substitute for the calcium in the organic salt other metals, but whilst they succeeded in this substitution in the case of barium they only obtained partial success with zinc, the experiments being carried out as follows:—

Fifteen grammes of gum free from sulphuric acid were dissolved in 150 c.c. of water and digested with 9 grammes of crystallized barium chloride. Alcohol was then added, giving a brown precipitate which was decanted with alcohol and carefully dried. This was then incinerated and the ash treated with sulphuric acid. The barium was then estimated by precipitation and also according to Carius's method to eliminate the error caused by small quantities of soluble sulphates, the average of the analyses showing 14·49 per cent of BaO. The sulphur contained was 7·77 per cent. The substance contained no chlorine. Zinc salt was obtained by dissolving 5 grammes of the gum in 100 c.c. of water and adding 2 grammes of zinc chloride. The ash from the precipitate with alcohol gave 6·95 per cent of ZnO and 7·86 per cent of S.

On comparing the three results the metals were found to be combined in almost molecular proportion. This leads to the conclusion that the precipitate obtained is the salt of a definite organic acid which is the principal constituent of the organic matter in the waste liquor, and which is produced by the action of the bisulphites upon the non-cellulose constituents of the wood. This supposition is further supported by the percentage of sulphur in the different precipitates, which when calculated in proportion to the molecular weight of the salt gives for the Ba salts 9·04 per cent; for the Ca salt 8·94 per cent; and for the Zn salt 8·44 per cent of sulphur, the average being 8·80 per cent.

Ten grammes of the organic barium salt were mixed with the calculated amount of sulphuric acid and the mixture was dissolved in excess of water. A small amount of $BaSO_4$ which was formed was filtered off. The mixture was allowed to stand for some days at a temperature of about 40° C., a white precipitate of $BaSO_4$ being gradually formed which was filtered off. This treatment was continued for about three weeks until no further precipitate was produced. No trace of either barium or sulphuric acid could then be detected in the liquid by the ordinary analytical methods. The solution was evaporated to a syrup, and alcohol added. No precipitate was obtained, showing that the pure organic acid was soluble in alcohol. A brown, flaky precipitate was obtained from this aqueous alcoholic solution by ether, and this was carefully dried. The amount obtained was about 3 grammes.

The substance thus purified is a brown, glossy, hydroscopic powder. It has an acid reaction, reduces Fehling's solution, yields with phenyl-hydrazine a yellowish-white precipitate, and gives precipitates with barium chloride and lead acetate which are soluble with difficulty. The ash, estimated as BaO, amounts to 1·26 per cent. The percentage of sulphur was 8·80 which corresponds with the amount obtained from the Ca, Ba, and Zn salts.

The average elementary composition, therefore, of the ash-free organic substance containing sulphur is

	(1) From Silesian waste liquors—	(2) From Austrian waste liquors—
C	53·29 per cent	56·27 per cent
H	5·23 "	5·87 "
S	8·80 "	5·52 "
O	32·29 "	32·24 "

consequently much more sulphur and less hydrogen and carbon are contained in the Silesian than in the Austrian waste liquor.

When allowed to stand for some months in the open air the sulphite liquor deposits $CaSO_4$ and turns lighter in colour. The dried substance obtained contains only 6·72 per cent of sulphur and the liquor itself contains 0·067 per cent of sulphur as sulphate. Oxidation of the organic matter has therefore taken place.

In the reduced solution left exposed in the open air a light yellow gum-like precipitate was thrown down with alcohol, containing 7·01 per cent of sulphur. On distilling with steam a milky liquid was obtained showing the same properties as the gas; it contains furfural. The quantities, however, show no definite proportion to the amount of waste liquor used.

Nitric acid acts energetically on the organic substance obtained from waste sulphite liquor. A considerable number of acids could be obtained, one of which was identified as oxalic acid.

The halogens have also an energetic action on waste liquor. With chlorine the liquor becomes blood-red, and yellow precipitate is produced which decomposes on heating, giving off HCl. It can be dried in a vacuum, is insoluble in water and alcohol, reduces Fehling's solution, and gives a brown precipitate with phenyl-hydrazine. On oxidizing with fuming nitric acid, chlorine and sulphur can be recognized. A remarkable occurrence in the sulphite-cellulose manufacture is a deposit of sulphur in the wooden pipes through which the waste liquor is discharged from the digesters. In these pipes a greyish-white crystalline substance is deposited which has the following composition: water, 6.28 per cent; $CaSO_4$, 87.41; FeO and Al_2O_3-0.13; silica 0.28; sulphur 5.75; total 99.85 per cent. The appearance of this sulphur shows that the SO^2 in the digester is not only oxidized but that some of it is reduced as well.

Mitt. Tech. Gew. Mus. (Vienna) vol. 7 (1897) p. 283.
J. Soc. Chem. Ind. vol. 17 (1898) p. 596.

Seidel, H. and Hanak, L.—WASTE SULPHITE LIQUOR.

In continuation of their previous work (see previous abstract) the authors now find that free furfural is a not inconsiderable constituent of the sulphite liquor, its presence being identified by extracting with ether, adding aniline, and, after evaporating the ether, adding hydrochloric acid, when the furfural reaction is distinctly obtained. Hence the previous statements require modification, since the whole of the furfural present does not originate from pentoses or pentosans. The presence of these substances is, however, proved by the phloroglucin reaction and by the fact that after distillation with hydrochloric acid the following substances gave furfural: thick liquor (sulphite liquor evaporated to 28° Bé), the solid precipitated by salt or by alcohol, the dry residue from the thick liquor, and finally the dry residue of the filtrate after precipitating with alcohol.

In order to remove sulphur from the organic substance contained in the liquor, the latter was treated with bleaching powder on the water-bath, filtered from gypsum, barium chloride added to the filtrate, the barium sulphate filtered off, and the solution evaporated. The product obtained is exceedingly hygroscopic, is free from sulphur, and reduced Fehling's solution strongly. The quantity of oxidizing agent necessary for this operation is too large to allow the method to be employed for rendering the sulphite liquor innocuous. Experimental evidence showed that chemical recovery of the sulphur is a simple matter, but the advantage could only be taken of this technically when it is possible to utilize the organic substance of the sulphite liquor for heating purposes. With regard to the reducing action of the sulphite liquor, this is not due to the sulphurous acid but to the organic substance containing sulphur. Sulphite liquor reduces completely Methylene Blue, Indophenol, and Indigo, and gives with 1.1 dinitnonapthalene a lilac, and with 1.4 derivative a brown dyestuff. A further use for sulphite liquor consists in employing the organic sulphur compound as a substitute for cream of tartar on alumina and chrome mordants of wool.

Mitt. Tech. Gew. Mus. (Vienna) vol. 8 (1898) (11 and 12) p. 337-347.
J. Soc. Chem. Ind. vol. 17 (1898) p. 863.

Seidel, H.—WASTE SULPHITE LIQUOR.

"In my last communication it was shown that the lignin substance of wood consisted of 64 per cent carbon, 6 per cent hydrogen, and 30 per cent oxygen.

"The data obtained by calculation from the different analyses of lignosulphonic acids showed differing values of the sulphur content, so that the composition of lignin was obtained by subtracting the amount of SO_2. The fact is emphasized that the above mentioned composition of lignin is that of the lignin which can be regenerated from the liquor. This lignin must differ from the original lignin of the wood by a greater content of hydroxyl groups. I assume that in the action of sulphurous acid on wood the following reaction takes place:—

$$X.\ CH:\ CH.–Y + SO_3\ H_2 = X.\ CH._2\ .\ CH.SO_3\ H:\ Y.$$

By heating at higher pressure the following decompositions occur:—

$$X.\ CH_2.\ CH.SO_3H.\ Y = X.\ CH_2.\ CHOH.\ Y + SO_2.$$

This decomposition is the reason why the waste liquor cannot be heated at higher pressures. The half of the organically-bound sulphur can be readily obtained as SO_2; alkaline heating at higher pressure is out of the question on account of the separation of $CaSO_3$. Calcium bisulphite waste liquor can be evaporated under reduced pressure or at atmospheric pressure at 100°–115° without decomposition of the lignin sulphonates.

"The regeneration of lignin from very dilute solutions of lignin sulphonic acid takes place very slowly and in small quantities at ordinary temperatures. If sulphite liquor is made weakly alkaline and allowed to stand several days a reversion of the reaction is observed."

The author's views on composition of lignin have received support from Klason (Kirchner, "Das Papier"). According to Klason, the chief substance of sulphite liquor, calcium lignin-sulphonate, has the composition $C_{18}H_{19}O_8SCa_{\frac{1}{2}}$. This corresponds to the percentage composition C. 54.5; H. 5.55; O. 32.32, for lignin sulphonic acid. These numbers also correspond with the numbers obtained by Lindsey and Tollens and by Seidel and Hanak. They give on subtracting for SO_2 the following as the composition of lignin:—

C. 65.06; H. 6.02; O. 28.91.

These differ considerably from Street's figures, viz:—

C. 64.54; H. 6.41; O. 29.06.

Z. angew. Chem. vol. 13 (1900) p. 1307.
Papier-Ztg. vol. 25 (1900) part II pp. 3295, 3371.
J. Soc. Chem. Ind. vol. 19 (1900) p. 1033.

Ahrens, F. B.—DISTILLATION EXPERIMENT WITH SULPHITE LIQUOR.

The liquor after the addition of infusorial earth was evaporated to dryness and then the residue, dried completely in air, was subjected to dry distillation. From 100 grammes there were produced 16-17 litres of gas (CO_2 heavy carbons, O, H, CH_4), and 50 grammes coke which contained 36 grammes infusorial earth. The heating value of the gas varied greatly, between 2,450 and 3,550 cals. The liquid distillate contained, besides a great deal of water, very small quantities of methyl alcohol and acetone, very small quantities of liquid hydrocarbons, and larger quantities of mercaptans.

Chem. Zeitschrift vol. 2 (1903) p. 743.
Chem. Zentr. (1903) part II p. 812.

SULPHITE PULP IN AMERICA:

Methods of manufacturing sulphite pulp at Ausable Forks, N.Y., on Lake Champlain.

Samples of waste liquor taken from digesters at end of the digestion process were found to contain 10·5 per cent solid material. About 90 per cent of this residue consists of organic and volatile matters, while about 5·7 per cent consists of calcium sulphate. When discharged into rivers the liquor is acid and contains 0·42 per cent calcium sulphate, the remainder being largely lignin and other organic extractions. It also contains finely divided wood-pulp.

Pulp Paper Mag. Can. vol. 4 (1906) p. 294.

Krause, H.—CHEMISTRY OF WASTE SULPHITE LIQUOR.

Sugar content.

Chem. Ind. vol. 29 (1906) p. 217.
Papier-Ztg. vol. 32 part I (1907) p. 1100.
J. Soc. Chem. Ind. vol. 25 (1906) p. 493.
Schwalbe. Lecture on Alcohol from Waste Liquor (Schwalbe 1910).

Krause, H.—CHEMISTRY OF SULPHITE LIQUOR.

The principal organic constituent of the waste lyes is the calcium salt of lignin-sulphonic acid, but corresponding to higher temperature of digestion the Ritter-Kellner liquor has a darker colour and contains more furfural and generally more sugars than the Mitscherlich liquor. Fehling's solution is not suitable for the detection of sugars in the liquors, since the lignin derivatives exert a reducing reaction even in the cold. Nylander's bismuth solution, however, is not reduced by the lignin bodies and can be employed for the detection of the sugars. The separation of the sugars is best effected by evaporating the liquor in the presence of barium carbonate to a pasty consistency, mixing the product with sand, and extracting the sugar by exhaustion three to six times with hot 90 per cent alcohol. The author's observation showed that in both processes of digestion the liquors from wood boiled in the autumn contained about twice as much sugar as those obtained in the spring. The waste liquors contain free furfural, pentosans, and pentoses; the lignin constituents of the liquors yield no furfural on distillation with hydrochloric acid. In addition to the pentosans and pentoses the liquors contain hexosans and hexoses. Amongst the sugars present the author has identified xylose, mannose, galactose, levulose, and traces of dextrose. The following table shows the results of analyses made of the two liquors obtained in the autumn by the two processes:—

—	Mitscherlich.	Ritter-Kellner.
	%	%
Furfural	0·01	0·02
Pentosans	0·40	0·29
Hexosans	0·21	0·49
Total sugars	1·48	1·47
Pentoses	0·47	0·41
Mannose	0·48	0·48
Levulose	0·28	0·25
Galactose	0·01	0·01
Dextrose	....	trace

The author has also investigated to a certain extent the lignin derivatives of the liquor. On the addition of bleaching powder to the liquor, acidified with hydrochloric acid, a chloro-derivative was obtained which, after purification by alcohol and ether, showed a composition corresponding with the formula, $C_{26}H_{29}ClSO_{32}$. This and other derivatives of lignin-sulphonic acid have the peculiarity of being soluble in alcohol only when acidified, whereas the presence of acid decreases their solubility in water. The author found that on boiling the liquors with dilute caustic potash the greater portion of the combined sulphur was split off without apparently any profound decomposition.

Chem. Ind. vol. 29 (1906) p. 217.
J. Soc. Chem. Ind. vol. 25 (1906) p. 493.

Frank, A.—COMPOSITION AND QUALITIES OF WASTE LIQUORS.

Kirchner, Das Papier vol. 2 (1907) p. 134.

DETERMINATION OF FREE AND COMBINED SULPHUROUS ACID IN WASTE LIQUORS.

Wochbl. Papierfabr. vol. 38 (1907) p. 3199.

Carlson, T.—THE POLLUTION OF THE MONDAL RIVER (SWEDEN) BY WASTE SULPHITE LIQUOR.

Amount and composition of the waste liquor. Based on 4·5 metric tons (4·96 short tons) cellulose, 1,050 kg. (2,310 lb.) inorganic and 4,405 kg. (9,700 lb.) organic substances.

Papier-Fabr. vol. 7 (1909) p. 587.
Papier-Ztg. vol. 35 (1910) part II p. 2117.

Kerp, W. and Wohler, P.—SULPHITE LIQUOR AND FURFURAL SULPHUROUS ACID.

The sulphur present in sulphite-cellulose waste lyes in the form of sulphurous acid (free and combined) amounts to one-fifth to one-third of the total sulphur. The proportion of sulphurous acid in the lyes which can be directly titrated with iodine increases with the dilution of the lye, and on continued titration with iodine the reaction proceeds in stages; these features are characteristic of the behaviour of sulphurous acid compounds of aldehyde. The combined sulphurous acid may therefore be considered to be present in the form of sulphurous acid compounds of the aldehyde consituents of the lye, viz. furfural, vanillin, xylose, mannose, galactose, and levulose. The lyes also contain a substance which, when the lyes are diluted, acts as an oxygen-carrier and exerts an oxidizing action on the sulphurous acid. The so-called calcium lignin-sulphonate must be regarded as a mixture of different substances. The reaction constant of the decomposition of sodium-furfural sulphite in aqueous solution is 0·72 x 10. In neutral solutions equilibrium is attained almost instantaneously, but less rapidly in acid solutions although the amount of decomposition is considerably greater in the latter case. Combination of sulphurous acid and furfural takes place only at the aldehyde grouping, not at the double linkage, furfural behaving in this respect as a saturated aldehyde.

Arbeit. Kais. Gesundh. vol. 32 (1909) p. 120.
Chem. Zentr. (1909) part II p. 710.
Papier-Fabr. vol. 7 (1909) pp. 45, 1135.
Papier-Ztg. vol. 34 (1909) p. 3286 vol. 35 (1910) p. 1932.
J. Soc. Chem. Ind. vol. 28 (1909) p. 1001.
Chem. Abs. vol. 4 (1910) p. 443.

Stutzer, A.—DETERMINATION OF SULPHUROUS ACID IN SULPHITE LYES.

The standard method for the determination of sulphurous acid in foodstuffs is to distil with a current of carbon dioxide together with steam in presence of phosphoric acid, collecting the vapours in iodine and weighing the sulphuric acid produced as barium sulphate. In this way are determined not only the inorganic sulphites but also the sulphurous acid held in combination with aldehydes and sugars. The waste lyes of sulphite wood-pulp mills contain, in addition to these forms of sulphurous acid, combined sulphurous acid in the form of calcium lignosulphonate, and when such lyes are treated with phosphoric acid in the manner described the results are variable according to the degree of decomposition undergone by the various organic derivatives of sulphurous acid present. The values obtained increase with the time of distillation and the concentration which the phosphoric acid thereby undergoes But in the analysis of waste sulphite pulp lyes it is for most purposes only of interest to determine the quantity of sulphurous acid which is readily split off under certain conceivable circumstances, whilst the more firmly fixed sulphurous acid may generally be considered as harmless. The author, therefore, proposes distillation with acetic acid instead of with phosphoric acid, the weaker acid readily decomposing the inorganic sulphites but only attacking the sulphurous in combination with aldehydes and lignin to a slight extent in a distillation of short duration. Two hundred and fifty c.c. of water are placed in an Erlenmeyer flask of 750 c.c capacity, the air expelled by carbon dioxide, and 25 c.c. of the waste sulphite lye are added with 25 c.c. of 25 per cent acetic acid. The liquid is kept in full ebullition for 15 minutes whilst the vapours are collected in iodine solution. This period of distillation is ample for the decomposition of sodium and calcium sulphites. Aldehyde sodium bisulphite is decomposed only to the extent of 4·8 per cent as against 22·8 per cent with phosphoric acid under similar conditions; calcium lignosulphonate is decomposed (using 50 c.c. of acetic acid) to the extent of 3·3 per cent.

Chem.-Ztg. vol. 34 (1910) p. 1167.
J. Soc. Chem. Ind. vol. 29 (1910) p. 1370.
Wochbl. Papierfabr. vol. 41 (1910) p. 4148.
Chem. Abs. vol. 5 (1911) p. 1335.

COMPOSITION OF WASTE LIQUOR AND WASH-WATER FROM SULPHITE MILLS.

Papier-Fabr. vol. 7 (1909) pp. 12, 136. 189.

Klason, P.—DISCUSSION ON KLASON'S PAPER ON "IRREGULAR PROGRESS OF SULPHITE COOKS".

Papier-Ztg. vol. 35 (1910) pp. 375, 451, 731.

Klason, P.—CONTRIBUTION TO THE KNOWLEDGE OF THE CHEMICAL COMPOSITION OF SPRUCE.

Investigations of the lignosulphonic acid contained in the waste liquor.

Gebr. Bornträger Berlin W. 35.
Pamphlet 2 of the German Association of Pulp and Paper Chemists.

Stutzer, A.—EXPERIMENTS ON WASTE SULPHITE LIQUOR.

Concentrated waste liquor (wood extract), cell-pitch, molasses, and waste liquor gave, when 100 grammes and 500 grammes of solid substance respectively were present in 1000 c.c. the following viscosity numbers (water = 100):—

	100 grammes in litre	500 grammes in litre
Wood extract..	120	402
Cell-pitch..	120	516
Molasses..	113	147

The unchanged liquor had the viscosity of 120. Molasses of 44·8° Bé is less viscous than wood extract of 32·5° Bé. The chemical analysis gave:—

	Wood extract	Cell-pitch	Original Liquor	Molasses
	%	%	%	%
Dry substance.	63·88	82·79	12·18	79·30
Crude ash..	2·64	14·70	1·44	11·81
Lime..	0·50	8·50	0·87	....
Total sulphur..	4·80	5·87	0·85	....
Sulphurous acid..	0·15	0·85	0·24	....
Calculated on 100 grammes dry substance				
Lime..	0·78	10·26	7·14	....
Total sulphur..	7·51	7·09	7·00	....
Sulphurous acid..	0·23	1·02	2·02	....
Crude ash..	4·13	17·99	11·82	....

The lignin had a specific gravity of 1·056. One hundred c.c. contained dry substance 12·87 grammes, ash 1·53 grammes, lime 0·92 grammes, sulphur 0·90 grammes, sulphurous acid 0·26 grammes.

Papier-Ztg. vol. 35 (1911) p. 5.
Jahrb. Chem. Techn. (1913) part II p. 501.

Schwalbe, C. G.—CHEMIE DER CELLULOSE.

This work contains information with regard to the composition of the liquor.

Berlin 1911 Gebr. Bornträger.

Honig, M.—ACETIC AND FORMIC ACIDS IN SULPHITE LIQUOR.

The waste liquors from the digestion of wood by the sulphite process contain acetic acid and formic acids, both in the free state and in combination with calcium; the proportion of free acid is always greater than that of the combined. In the waste liquors examined by the author the total quantity of acetic and formic acids found ranged from 2·151 to 9·078 grammes per litre. On the assumption that 1 cubic metre (35·3 cubic feet) of waste liquor corresponds to 100 kilogrammes (220 lb.) of cellulose, the daily production of volatile organic acids in a wood-pulp mill may be calculated. If 100 kilogrammes (220 lb.) of cellulose are assumed to be derived from 300 kilogrammes (660 lb.) of raw wood, the yield of volatile acids works out at from 0·72 to 3·03 per cent of the weight of the wood. The proportion of formic to acetic acid varies according to the circumstances; in two liquors it was 1:5·78 and 1:5·60, whilst in a third it was 1:13·6. In the analysis of the liquors for the separation of the volatile acids, the vapours produced in the distillation, before they enter the condenser are passed through a flask containing a milk of calcium or barium carbonate maintained in gentle ebullition. In this way a complete separation of the organic acids from the volatile aldehydes is effected whilst most of the sulphurous acid is precipitated. The solution containing the salts of the organic acids is filtered, concentrated to 100 c.c., treated in the cold for 4 hours with a little hydrogen peroxide to oxidize the residue of sulphurous acid, and the excess of peroxide destroyed by manganese or lead peroxide. The solution is divided into two parts, in one of which the total volatile acid is determined, and in the other the formic acid is determined, gravimetrically by mercuric chloride and sodium acetate. If a solution of the neutral lead salts be evaporated and the residue extracted with alcohol the lead formate remains insoluble, whilst the soluble portion contains the acetate; no other volatile organic acids are present.

J. Soc. Chem. Ind. vol. 31 (1912) p. 768.
Chem.-Ztg. vol. 36 (1912) p. 889.
Chem. Abs. vol. 6 (1912) p. 3517.
Paper vol. 9 (1912) No. 1 p. 29.

Zweiberg, G. von.—TESTING OF SULPHITE CELLULOSE LYES WITH IODINE.

The titration of the sulphur dioxide in sulphite digestion liquors, by means of iodine, may lead to erroneous results unless certain precautions be taken. The principal sources of error are loss of sulphur dioxide by volatilization and the reversibility of the reaction; $SO_2+H_2O+21=2HI+SO_3$. The latter error is diminished by working at high dilutions. If iodine be added to a strong solution of sulphurous acid the reaction may also be complicated by the liberation of sulphur. Excessive stirring and exposure to air is to be avoided. The best method is to dilute the sulphite liquor to a concentration approximately equivalent to that of the iodine, and to run the sulphite solution into the iodine so that an excess of the latter is present until the end. For the separate titration of the free and combined sulphurous acid, the acid produced by the reaction with iodine must be titrated subsequently with sodium hydroxide. For the combined titration, 2 c.c. of the sulphite liquor are diluted with 20 c.c. of water and run in a fine stream into 10 c.c. of N/8 iodine solution; starch should be added only towards the end of the titration; when decoloration is complete 2 drops of phenolphthalein are added and the liquid is titrated with N/8 sodium hydroxide. For the titration of the sulphur dioxide at the end of the boiling process, 100 c.c. of lye are made alkaline with a solution of lime and sugar, then boiled and filtered; the precipitate is dissolved in hydrochloric acid, diluted to 250 c.c., and 25 c.c. are taken for titration with iodine. Alternatively 25 c.c. of lye may be distilled in an atmosphere of carbon dioxide with 25 c.c. of 25 per cent acetic acid and 250 c.c. of water, and the distillate collected in N/10 iodine.

Svensk Pap. Tid. (1913) May 31.
Papier-Fabr. vol. 11 (1913) p. 1007.
Paper vol. 12 (1913) No. 13 p. 15.
J. Soc. Chem. Ind. vol. 32 (1913) p. 863.
Chem. Abs. vol. 7 (1913) p. 3837.
Pulp Paper Mag. Can. vol. 11 (1913) p. 52.

Walker, W. O.—THE PROBLEM OF THE WASTE LIQUOR FROM SULPHITE MILLS.

Composition of the digester liquor. As it comes from the digester it is a dark reddish-brown liquid of variable specific gravity, about 1.05. It has a peculiar, not unpleasant odour, due to bodies of a terpent nature. By evaporation of the liquor a syrup is obtained which, on further evaporation, changes to a glue-like mass. The dried residue is about 10 to 12 per cent of the weight of the original liquor. This residue on ignition gives about 12 per cent of ash, chiefly sulphates of calcium and magnesium. The other 88 per cent is organic material.

The following substances have been shown to be present in the liquor: Chief constituent an organic sulphur compound, probably a calcium and magnesium sulphonate; small quantities of sulphurous acid, pentoses and pentosans, a terpene-like substance and free sulphur; very small quantities of sulphuric acid, mannose, dextrose, and galactose; free furfural and traces of vanillin or vanillin-like body.

The chief constituent of this liquor may be precipitated by alcohol and is obtained thereby as a dark, gummy mass which becomes brittle by drying.

It is also obtained by concentration and salting out by means of sodium chloride or magnesium sulphate. Purification is difficult as it is apparently only soluble in water and dilute alcohol from which it does not crystallize. It yields chlorine and bromine derivatives, contains active carbonyl and methyl groups, and is a strong reducing agent. Sulphur in the compound is shown by McRae to be present in the form of a sulphonic group. It is probably the soluble reaction product from the calcium and magnesium bisulphites on the complex groups in combination with the cellulose in the lignocelluloses. These groups are commonly called lignin or lignone and have the characteristics of di-ketones, particularly quinones. The lignone complex contains more carbon than cellulose. The lignone-bisulphite compounds have been separated in various derivative forms and analysed. The product precipitated by hydrochloric acid from the waste liquor has been given the empirical formula $C_{24}H_{24}(CH_3)_2SO_{12}$ and the formula $C_{24}H_{24}(CH_3)_2O_{10}$ to the parent lignone complex,

Our structural knowledge of the lignone group is very limited and has been gathered from complex decomposition reactions. These reactions show the presence of hydrocarbon nuclei of very small dimensions together with a high proportion of CO groups alternating in periods of short dimensions with the hydrocarbon groups. Furfural derivatives appear to be present, also CH_3 groups and a low proportion of OH groups.

J. Soc. Chem. Eng. vol. 32 (1913) p. 389.
Chem. Eng. vol. 17 (1913) p. 246.

Schwalbe, C. G. and Grimm, H.—ROSIN IN WASTE SULPHITE LIQUOR

Less than 0·03 per cent rosin could be extracted by shaking with ether.

Wochbl. Papierfabr. vol. 44 (1913) p. 3251.
Chem. Abs. vol. 7 (1913) p. 3837.

Honig, M.—FORMIC ACID AND ACETIC IN WASTE SULPHITE LIQUORS.

Author states that no organic acids other than formic and acetic acid are contained in the waste liquors. In 1 litre liquor 2·151 grammes up to 9·078 grammes of volatile organic acids were found.

Chem.-Ztg. vol. 36 (1912) p. 889.
Chem. Abs. vol. 6 (1912) p. 3517.
Paper-Maker Brit. Trade J. (1915) p. 497.

Kerp, W. and Wohler, P.—TO THE KNOWLEDGE OF COMBINED SULPHUROUS ACID.

Sulphite pulp and furfural sulphurous acid. A chemical and pharmacological investigation.

Papier-Ztg. vol. 38 (1913) p. 3063.
Arbeit. Kais. Gesundh. vol. 32 p. 120.

Banthier, G.—DECOMPOSITION OF CELLULOSE, STARCH, SUGAR, AND SULPHITE BY HEAT.

The behaviour on dry distillation of cellulose, starch, and sugar substances, having the same percentage composition, was compared by heating under the same conditions in an iron retort 44 cm. long and 6.5 cm. in diameter, arranged in an electrically heated oven. A length of 21 cm. of the retort was charged with the material and the temperature was raised gradually so as to reach 100° C. in 1½ hours and 500° C. in 7 or 8 hours. The products of distillation in percentage by weight of the dry substances were as follows:—

—	Cellulose.	Starch.	Sugar.
	%	%	%
Coke	32·9	28·6	12·2
Water	31·7	29·7	6·29
Tar	3·25	2·69	55·04
Acetic acid	3·28	5·29	8·78
Aldehydes	5·82	5·66	6·15
Ketones	0·11	1·11	0·34
Total gases	17·33	22·70	5·96
Carbon dioxide	11·26	13·08	4·37
Ethylene	0·24	0·39	0·05
Hydrogen	0·02	0·03	0·01
Carbon monoxide	4·78	7·64	1·29
Ethane	0·35	0·74	0·11
Methane	0·68	0·82	0·13
Loss or undetermines	5·23	4·20	5·38
Composition of tar—			
Carbon	52·20	45·02	38·91
Hydrogen	6·86	6·31	6·19
Oxygen	40·94	48·67	54·90

The time-temperature curves showed that with cellulose an exothermic decomposition takes place between 250° and 300°C, and that this reaction is complete at 320°C. This phenomenon is not shown by starch and sugar. The stability towards heat increases in the order: cellulose, starch, sugar; but the first two are more nearly alike in this respect than either is to sugar. Since cellulose does not yield methyl alcohol on dry distillation, it has been supposed that waste sulphite-cellulose lyes contain the constituents of wood which yield valuable distillation products. The lye was therefore partially separated from sulphur compounds by passing through it a current of air and steam, evaporated to dryness and distilled. A very small yield of liquid products was obtained and no methyl alcohol, whilst large quantities of hydrogen sulphide and mercaptan were evolved.

J. Gasbel. vol 57 (1914) 32 and 55.
J. Soc. Chem. Ind. vol 33 (1914) p. 129.
Chem. Abs. vol. 8 (1914) p. 1344.

Klason, P. and Segerfeld.—BORNEOL IN SULPHITE LIQUOR.

During rectification of alcohol obtained from waste liquor a reddish-brown oil separated out. From this oil optically inactive borneol, similar to that resulting from treatment of turpentine with concentrated sulphuric acid, was recovered. The borneol was probably formed in the digestion process from bornyl acetate (or similar ester) originally present in the volatile oils of the wood.

Svensk Kem. Tid.
Paper vol. 13 (1914) No. 18 p. 18.
Chem. Abs. vol. 8 (1914) p. 1345.

Bergstrom, H. O. V.—INACTIVE BORNEOL FORMED IN THE SULPHITE PROCESS.

Papier-Fabr. vol. 13 (1915) p. 229.
Chem. Abs. vol. 9 (1915) p. 2709.
J. Ind. Eng. Chem. vol. 7 (1915) p. 999.
Paper vol. 16 (1915) No. 7 p. 18.

Hagglund, E.—DIE SULFITABLAUGE UND IHRE VERARBEITUNG AUR ALKOHOL. (WASTE SULPHITE LIQUOR AND ITS CONVERSION INTO ALCOHOL.)

Gives a discussion of the composition of the waste liquor.
Fr. Vieweg. Sohn. Braunschweig (Germany) (1915) p. 56.

Hagglund, E.—CARBOHYDRATES OF PINE WOOD.

Sulphite liquors contain 2·3 per cent sugar consisting of 0·71 per cent xylose; 1·04 per cent mannose; 0·06 per cent galactose; 0·06 per cent fructose; 0·43 per cent undetermined. Of the total sugar 30 per cent is xylose; 41·7 per cent mannose; 2·6 per cent, galactose; and 3·0 per cent, fructose.

If the wood is hydrolyzed with 0·5 per cent H_2SO_4 at 155° or 170° for 30-45 minutes, part of the cellulose is hydrolyzed so that glucose is present in the sugar mixture. The amount of sugar is 9 per cent or 14·5 per cent of the dry weight, depending on the temperature. The various sugars were:—

—	At 155°.	At 170°.
	per cent.	per cent.
Xylose	32·7	30·1
Mannose	35·6	43·7
Fructose	4·3	4·7
Galactose	3·3	3·3
Glucose	0·5	14·0
Undetermined	23·6	4·2

Chem.-Ztg. vol. 70 (1915) p. 416.
Chem. Abs. vol. 9 (1915) p. 2925.

Oman, E.—THE AMMONIA TEST FOR SULPHITE LYES.

Papier-Fabr. vol. 14 (1916) p. 509.
Tekn. Tid. vol. 46 (1916) p. 4.
J. Soc. Chem. Ind. vol. 35 (1916) p. 832.
Chem. Abs. vol. 10 (1916) p. 2636.

Hagglund, E.—ANALYSIS OF CALCIUM HYDROGEN SULPHITE SOLUTION

Chem.-Ztg. vol. 40 (1916) p. 433.
J. Soc. Chem. Ind. vol. 35 (1916) p. 686.
Chem. Abs. vol. 10 (1916) p. 2636.

Oman, E.—SUGAR FORMATION IN THE SULPHITE PROCESS.

At the beginning of the cook the lye contains a large proportion of non-hydrolyzed sugar. The non-hydrolyzed sugar is split up by the acid liquor during the progress of the cook, but it is by no means always completely hydrolyzed.

Tekn. Tid. vol. 46 (1916) p. 6.
Papier-Fabr. vol. 14 (1916) pp. 256, 273, 291, 306, 485, 584.
J. Soc. Chem. Ind. vol. 35 (1916) p. 832.
Chem. Abs. vol. 10 (1916) p. 2637

Hagglund, E.—SUGAR FORMATION IN THE SULPHITE PROCESS. (Reply to Oman.)

Papier-Fabr. vol. 14 (1916) pp. 353, 570.

Klason, P.—REPLY TO OMAN'S ARTICLES ON SUGAR FORMATION AND "BLACK COOKS."

Papier-Fabr. vol. 14 (1916) p. 657.

Klason, P.—ANALYSIS OF SULPHITE LIQUOR.

Discusses Oman's investigations on this subject especially the ammonia test.

Svensk Pap. Tid. vol. 19 (1916) p. 115.
Papier-Fabr. vol. 14 (1916) p. 739.

Oman, E.—ANALYSIS OF SULPHITE LIQUOR (REPLY TO KLASON).

Svensk. Pap. Tid. vol. 19 (1916) p. 143.

Dieckmann, R. and Hagglund, E.—THE ANALYSIS OF SULPHITE LIQUOR.

Chem.-Ztg. vol. 40 (1916) p. 581.
Chem. Abs. vol. 11 (1917) p. 1544.

Kertesq, Z.—VOLATILE ORGANIC COMPOUNDS FORMED IN THE SULPHITE PROCESS.

The relief gases carry off acetaldehyde, acetone, methyl alcohol, acetic and formic acids, and furfural. One thousand litres (220 gallons) waste liquor yield about 0·6 litre (0·13 gallons) acetaldehyde, 0·2 kg. (0·44 lb.) acetone, 0·53 kg. (1·17 lb.) methyl alcohol and 6.32 kg. (13.9 lb.) ethyl alcohol. The essential oils which collected on the surface of the liquor were separated into 80 per cent cymene, 10-12 per cent sesquiterpene, about 4-5 per cent diterpene, and traces of polyterpene.

Chem.-Ztg. vol. 40 (1916) p. 945.
Chem. Abs. vol. 12 (1917) p. 1040.
Paper-Maker Brit. Trade J. (1917) vol. 52 p. 36.
Pulp Paper Mag. Can. vol. 15 (1917) pp. 236, 306.

Dickerson, W. H.—THE DISPOSAL OF WASTE SULPHITE LIQUOR.

Discussion at the meeting of the American Technical Association of the Pulp and Paper Industry. Great variations in inorganic matters 5-10 grammes CaO and MgO per litre; specific gravity about 5°-8° Bé. The ratio of inorganic material to the organic is on an average 15 per cent. By draining the blow-pits, approximately 1,500 pounds of solids should be obtained per ton of pulp (up to 2,100 pounds by special apparatus).

Paper vol. 19 (1917) No. 20 p. 19.

Klason, P.—THE SUGARS IN WASTE SULPHITE LIQUOR.

Referring to Hagglund's work, Klason states that the fermentable sugar originates from the carbohydrates which are present in the wood to an amount of 16 per cent. Two liquors of specific gravity 1.052 and 1.0504 and dry substance 13.5 per cent and 11.5 per cent were examined. Sulphurous acid titrated with iodine 0.26 and 0.13 per cent, lime content 0.75 per cent and 0.82 per cent. The total sugar in the liquor is between 3.3 and 3.6 per cent as follows: mannose, 0.526 per cent; galactose, 0.279 per cent; glucose, 1.65 per cent; arabinose, 0.90 per cent. Glucose and mannose are more easily fermentable than galactose. The usual yield of alcohol from the liquor is 1 per cent by volume, maximum yield 1.4 per cent.

Svensk Pap. Tid. vol. 20 (1917) p. 176.
(See " Alcohol " p. 105.

EFFLUENTS

The sulphite mills situated on large rivers or seas usually have the great advantage of being allowed to discharge the waste liquor without any previous purification. In Canada with her large rivers and sparse population the problem of the disposal of waste liquor waters has not, therefore, been so widely discussed.

However, in densely populated countries where legislation prohibits the direct emptying of the waste liquors into the streams the sulphite-pulp industry meets with great difficulties. In some districts mills are even forced to close down if they are unable to dispose of the liquor in a satisfactory manner. In fact the great development of processes for utilization of the waste sulphite liquor is due more to these circumstances than to efforts on the part of the manufacturers to turn the enormous quantities of valuable material wasted in this process into useful products. The available literature on the question of the pollution of rivers by sulphite liquor and the purification of the liquor shows that there is some difference of opinion regarding the injuriousness of the liquor, caused by fibres, sulphurous acid, and dissolved organic substances.

It has been pointed out that the fibres collect in the river and precipitate impurities from the effluents of other factories and from sewage, forming a mud at the bottom of the river, poisoning the fish, and causing other damage. The fibre losses from the mills are often very large, but the fact that these vary between 1 and 10 per cent of the dry pulp produced shows that it is possible, by the use of effective save-alls, to decrease the losses considerably in some mills. This is especially desirable as it would mean a recovery of very valuable material. The fibres lost do not, as it is generally believed, consist chiefly of the less valuable parenchyma cells but contain a large proportion of good tracheids. The fibres are largely absorbed by the layer of algae and also form a nutriment for organisms. The growth of algae is considerably increased by the organic substances of the waste liquor, particularly the fermentable sugars. The algae usually present in the rivers are of a brownish colour and are attached loosely to the river-bed but are changed into a stronger structure of a greyish colour by the action of the sulphite liquor. In small rivers, and especially where the water flows slowly, the growth of algae caused by the organic matters of the liquor may be so considerable that the whole river-bed is practically covered with a layer of algae, preventing the fish from reaching the nutriment of the soil. Large proportions of the algae die and give rise to the bad odours often noticed. It has been considered of importance to remove as far as possible the free or loosely-combined SO_2 from the liquor before discharge, and a neutralization of the liquor has been recommended. On the other hand it has been stated that a neutral or slightly alkaline liquor is more harmful as regards growth of algae than is the acid liquor. No doubt the organic substances directly favour the growth of algae and in small rivers or rivers with a slow current this has an injurious effect upon fish life, but it is also stated that a certain fish nutriment is developed through the influence of the organic substances. The former was the case in Konigsberg (Germany) where the liquor had to be taken in tank steamers and discharged in the open sea. The free sulphurous acid present in the liquor requires for its oxidation a certain amount of oxygen, which in rivers that are not sufficiently aerated has to be supplied by the water itself. In small rivers the fish may in this way be deprived of the oxygen required for respiration. Indirectly the sulphur content of the liquor may have an injurious effect upon fish life through the decomposition of sulphates and the subsequent formation of hydrogen sulphide.

For the purification of waste liquor several methods have been proposed. A high dilution with water as obtained in large rivers is no doubt very effective as far as the oxidation of the reducing substances of the liquor is concerned, but the increased growth of algae caused by the organic substances is noticed even in high dilution if the liquor is added continually to the stream. But this alga (*Sphaerotilus*) is very sensitive towards any interruption in the food supply and, recognizing this fact, it has been proposed to discharge the liquor intermittently, e.g. twice in 24 hours. In some cases this has proved to be of benefit. Biological treatment has apparently not been successful because of the antiseptic action of the sulphurous acid. Irrigation does not effect the necessary purification except in cases where the liquor has previously been mixed with sewer effluents from a city. Oxidation of the liquor before discharge into the river has proved inefficient. The purification of the rivers by copper sulphate has also been considered, but it has been pointed out that this treatment will also destroy such algae as are necessary in the river for the production of oxygen and the absorption of organic substances from waste effluents. Copper sulphate is also changed chemically by the action of the carbon dioxide present in the water. The copper carbonate, however, does not act upon the fungus but precipitates in the sludge, and may in this way be injurious to the natural fauna of the river.

Although it appears that no effective purification can be obtained in a simple manner and therefore the expensive evaporation of the liquor in some cases may prove to be the only possible method for its disposal, the modern processes for utilization of waste sulphite liquor, e.g. the production of alcohol, tannin extract, binding material, and fuel may satisfactorily solve the problem of river pollution by waste sulphite liquor.

Mitscherlich, A.—IMPROVEMENTS IN THE PROCESS OF, AND APPARATUS FOR BOILING WOOD WITH SULPHITES.

Description of the most important points of the process and method of preventing the spent liquors from being obnoxious, by discharging the same through iron pipes into collecting tanks containing cold liquid and then causing the same to mix with about one thousand times their volume of water.

English Patent 1655 (1884).
J. Soc. Chem. Ind. vol. 4 (1885) p. 549.

Leisenberg, C.—PROCESS FOR PURIFICATION OF EFFLUENTS BY ALKALI FERRITES OR ALKALI FERRITE ALUMINATES.

The sodium ferrite is made by heating an iron ore or a mineral containing iron, e.g. bauxite with sodium carbonate in a muffle. The waste water is first made slightly alkaline with lime and then the ferrite is added, iron hydroxide separates preventing formation of H_2S and carries down much of the inorganic and organic substances present.

German Patent 37882 (1886).
Ber. (1887) p. 30.
Papier-Ztg. vol. 12 (1887) p. 398.

Korndorff, Th.—PROCESS FOR PURIFICATION OF EFFLUENTS WITH CHARCOAL SATURATED WITH CHLORINE.

German Patent 32696 K.L. 12 (1886).
Papier-Ztg. vol. 11 (1886) p. 1419.

Konig, J.—POLLUTION OF WATER AND DANGEROUS CONSEQUENCES.

Methods of Purification of Effluents.
Jul. Springer, Berlin (1887).
Chem.-Ztg. vol. 11 (1887) p. 1111.

PURIFICATION OF EFFLUENTS.

Statement regarding dilution of waste water when discharged into the rivers.
English Bill of August 18, 1886.
Papier-Ztg. vol. 12 (1887) p. 770.

Schreib, H.—PURIFICATION OF EFFLUENTS.

Action of calcium hydroxide upon the organic substances in the waste water.
Papier-Ztg. vol. 12 (1888) p. 1489.

Frank, A.—PURIFICATION OF EFFLUENTS.

Frank is opposed to the use of processes in which the liquor trickles over limestone. Injurious substances can only be removed completely through the use of caustic lime.
Papier-Ztg. vol. 14 (1889) p. 1488.

Frank, A.—PROCESS FOR PURIFICATION OF EFFLUENTS FROM SULPHITE MILLS BY FILTRATION OF IRRIGATION FIELDS.

Only the removal of directly injurious substances from the liquor is necessary, whereas substances as sugar, amyloids, etc., are removed by self-purification in the river.
Papier-Ztg. vol. 14 (1889) p. 383.
Hofmann C.: Handbuch der Papierfabrikation, 2nd edition (1897) p. 1597.
Schubert, Zellstoffabrikation (1906) pp. 256, 266.

Gottstein, L.—PURIFICATION OF EFFLUENTS.

Some success has been obtained by allowing the liquor to trickle over limestone. The formation of certain algae has been prevented.
Papier-Ztg. vol. 14 (1889) p. 1556.

OPPERMANN'S PROCESS FOR PURIFICATION.

To prevent the development of lower organisms in waste waters, ozonized dolomite or magnesia lime is used. Sugar and gum substances remain in solution.
Papier-Ztg. vol. 14 (1889) pp. 1512, 1735.

Schreib, H.—FORMATION AND NATURE OF FUNGI TROUBLES.

The lime that remains dissolved in the settled liquors is not injurious.
Papier-Ztg. vol. 14 (1899) pp. 1576, 1875.

Webster, M.—PURIFICATION OF EFFLUENTS WITH ELECTRIC CURRENT.
Papier-Ztg. vol. 14 (1889) p. 1312.

Haussner, A.—NEW FEATURES IN PAPER MANUFACTURE.

The author refers to Frank's process for purification of waste liquor. The liquor is mixed in tanks with the gases from the digester and then with milk of lime; $CaSO_3$ is precipitated and is used again. The clear liquid is then treated with air for the separation of the lime. Webster has proposed a purification by means of electric current.
Dingler's polytechn. J. vol. 275 p. 577, vol. 276 p. 49, vol. 277, pp. 118, 174, 211.
Jahrb. Chem. Techn. (1890) p. 2876.

Schreib, H.—EFFLUENTS.
Z. angew Chem. Vol. 3 (1890) p. 675.

Durr & Co.—PROCESS FOR REMOVAL OF ACID FROM WASTE LIQUOR AT THE END OF THE "COOK".

The liquor is subjected to evaporation at a very much diminished pressure.
German Patent 71942 (1893).
Ber. vol. 27 (1894) p. 220.

SULPHITE WOOD LIQUORS AND POLLUTIONS.

Several paper-mills in the Breslau and Liegnitz districts have made serious attempts to minimize the pollution occasioned by the discharge of sulphite liquors.

Neutralization with lime followed by settling, addition of lime in excess, and filtering off the precipitated sulphite, and variation of such treatments, have given only partial results. Two mills have adopted the drastic process of evaporation to dryness and calcining the residue, which appears for the moment to be the only effectual solution of the problem.
Papier-Ztg. vol. 17 (1892) p. 2148.
J. Soc. Chem. Ind. vol. 12 (1893) p. 58.

Bruck, E.—TREATMENT OF WASTE LIQUORS FROM THE BISULPHITE PROCESS.

The author proposes to treat these liquors with gelatin and alum for the removal of the soluble lignone derivatives and subsequently with chalk to neutralize. This treatment is found to remove one-fourth of the dissolved organic matter and a large proportion of the uncombined sulphite, and to give an effluent which remains unchanged for months.
Chem.-Ztg. vol. 95 (1892) p. 1782.
J. Soc. Chem. Ind. vol. 12 (1893) p. 460.

Carpenter and Schulze.—PROCESS FOR REMOVAL OF ACID FROM WASTE LIQUOR AT THE END OF THE "COOK".

Warm compressed air is forced through the pulp, whereby oxidation products are formed which would only have been formed in the waste liquor by atmospheric oxidation.
German Patent 78306 (1894).
(Addition to German Patent 71942.)
Ber. vol 28 (1896) p. 260.

Wichelhaus, H.—EXAMINATION OF WASTE SULPHITE LIQUORS AND EFFLUENTS FROM SULPHITE MILLS.

Methods for purification. Removal of sulphurous acid by neutralization with lime and oxidation of the organic substances by air.
Chem. Ind. vol. 18 (1895) p. 51.
Papier-Ztg. vol. 20 (1895) p. 1180.
Hofmann, C., Handbuch der Papierfabrikation, 2nd edition (1897) p. 1622.
Chem.-Ztg. vol. 19 (1895) p. 46.

Ekman, C. D.—WASTE SULPHITE LIQUOR.

Review of methods of utilization. Irrigation has proved unsatisfactory. The decomposed or oxidized liquor finds its way to the water-courses of the neighbourhood in the form of a dark liquor of disagreeable odour. The best method is to dilute the liquor at once with as much water as possible before it goes into the river. If no large river or sea is close at hand the best method is to evaporate the liquor and condense the steam so as to prevent pollution of the air.
Papier-Ztg. vol. 21 (1896) part I pp. 2218, 2609, 3247.
J. Soc. Chem. Ind. vol. 15 (1896) p. 735.

Hofmann, C.—HANDBUCH DER PAPIERFABRIKATION.
Second edition (1897) p. 1622.

Schnarmann, H.

The erection of a plant at Unterkochen for preparation of Ekman's "dextrone" was forbidden because of the nature of the residual liquor.
Papier-Ztg. vol. 22 (1897) part II p. 3679.

Spindler, H.—PURIFICATION OF SULPHITE LIQUORS.

The destruction of the organic substances is not complete even with energetic oxidation.
Chem.-Ztg. vol. 21 (1897) p. 302.

Pollacsek, E.—PROCESS FOR PURIFICATION AND UTILIZATION OF EFFLUENTS FROM SULPHITE MILLS.

Oxidation with air and iron chloride.

Austrian Privilegium 967 (1898).
(See "Miscellaneous" p. 168.)

Goldschmidt, E.—ACTION OF FORMALDEHYDE ON SULPHITE LIQUOR.

Spent sulphite lyes heated in hydrochloric acid solution with excess of formaldehyde give a brown precipitate of methylene compounds of sugars; it may be prepared pure through the benzoyl compound. Formaldehyde is worthy of attention as a means of purifiying these waste lyes; it fixes the sulphurous acid and prevents excessive growth of moulds and algae.

Chem.-Ztg. vol. 22 (1898) p. 374.
J. Soc. Chem. Ind. vol. 17 (1898) p. 790.

DISPOSAL OF SULPHITE CELLULOSE WASTE LIQUORS.

The offer of a sum of money for a process of rendering harmless the waste liquors of the paper and cellulose factories of Unterkochen and Wolfash resulted in 83 applications of which 75 were German, the remainder being from America, England, Sweden, Norway, and Austria-Hungary. Besides the prize given for the process selected a further sum was given to the inventors of the next best process, and three other processes were considered worthy of attention. In very many cases suggestions were made which had already been tried and found to be impracticable. Many of the proposed processes failed to take into account the local conditions of the factories; others were obviously useless or else introduced other inconveniences. L. J. Dorenfeldt received the first prize, Drs. Appel and Max Buchner the second prize, and Dr. Oesterlen and Assistant Inspector Honold of Stuttgart with Drs. Kuehn and Gilg received honourable mention.

Papier-Ztg. vol. 23 (1898) p. 3527.
J. Soc. Chem. Ind. vol. 17 (1898) p. 1171.

Schikora.—FISH EAT WATER FUNGI.

Z. Fischerei (1899) part I p. 5.

Banning and Setz.—SETTLING ARRANGEMENT FOR WASTE WATER.

D.R.G.M. 132826 (1900).

Weigelt, C.—EXAMINATION OF EFFLUENTS AND FISH WATERS.

Edited by Deutsch Fischereiverein, Berlin 1900.

Ferenczi, S.—PURIFICATION OF WATER.

Papier-Ztg. vol. 26 (1901) p. 271.

Fischer, F.—DAS WASSER.

Jul. Springer, Berlin (1902).

Stutzer, A.—ACTION OF SULPHUROUS ACID AND OTHER SUBSTANCES OF SULPHITE LIQUORS ON PLANTS.

The author's experiments have shown that sulphurous acid is extremely injurious to plants that grow in water. Hence, when sulphite lyes are discharged into small rivers the plants on the banks turn yellow or perish completely. In further experiments it was found that under the conditions chosen the influence of sodium bisulphite upon the germination process was only slightly weakened by the presence of potassium carbonate. The latter salt, however, was able to strengthen germinated plants, so that taking an approximately equal number of plants the production of green leaves, etc., rose from 211 to 275 grammes. The author concludes that the sodium bisulphite gradually reacts with the constituents of the soil to form less injurious compounds, and that this change is accelerated by the presence of calcium carbonate. Neutral compounds of sulphurous acid that are only sparingly soluble in water are much less dangerous to plants than the readily soluble salts. Neutral potassium sulphite is soluble in 800 parts of water.

On mixing sulphite lyes, concentrated by evaporation, with an equal weight of powdered Thomas slag and evaporating the mixture the amount of sulphurous acid fell to 1 or 2 parts per 1,000 and the lime in the Thomas slag converted this residue of sulphurous acid into neutral calcium sulphate. Similar results were obtained in the actual experiments of plants.

D. Landw. Presse vol. 29 (1903) p. 725.
J. Soc. Chem. Ind. vol. 22 (1903) p. 42.

Vogel, J. H.—PAPER-MILL AND PULP-MILL EFFLUENTS.

The effluents from sulphite wood-pulp mills are very objectionable, and no satisfactory process exists for their purification. These liquors contain, in addition to the sulphur derivatives, considerable quantities of sugar which afford nutriment for the growth of a fungus, *Sphaerotilus natans,* in the streams. Hofer has shown that it is the fermentable hexose sugars, principally, which give rise to its growth. Numerous attempts have been made to treat the liquors by the same process as is employed for the bacterial purification of sewage, but the sulphur compounds have such an inhibitive action on the bacteria that no purification is effected in the beds. The author thinks, however, that if the liquors were first treated for the precipitation of sulphites and were then subjected to putrefaction in a septic tank, with the addition of seepage, something might be effected by this process. Some mills dilute their liquors and run the effluents day and night into the stream; but Hofer considers that less harm is done by discharging the whole of the liquors at once, intermittently, provided the stream is a large one, since the fungus growths are thereby nourished for a shorter time. The so-called continuous settling arrangements do not remove the suspended matters so efficiently as sedimentation in tanks; in these, after 12-15 hours, the liquor only contains 10-12 milligrammes of suspended matter per litre. In soda-pulp mills, only the more dilute washings, containing 10 per cent of the total wastes, have to be discharged. In small streams these liquors give rise to the accumulation of algae. They should, however, be quite amenable to treatment on the bacterial system after a preliminary putrefaction in a septic tank, which would also serve for the removal of the fibrous matters by sedimentation.

Wochbl. Papierfabr. vol. 37 (1906) p. 1612.
Papier-Ztg. vol. 31 (1906) pp. 1278, 1314 and 1355.
J. Soc. Chem. Ind. vol. 25 (1906) p. 555.

Gottstein, L.—ON SULPHITE LIQUOR.

According to experiments of the Bavarian Fishery Experimental Station it is preferable to run the liquor into the streams intermittently rather than continuously.

Remarks to Klemm.

Papier-Ztg. vol. 31 (1906) p. 952.
Z. angew. Chem. vol. 19 (1906) p. 1270.

Klemm, P.—WATER AND EFFLUENTS.

Lecture to the Pulp and Paper Chemists.
Papier-Ztg. vol. 31 (1906) p. 694.
Z. angew. Chem. vol. 19 (1906) p. 293.

Ramsay, W.—PURIFICATION OF EFFLUENTS.

Z. angew. Chem. vol. 19 (1906) p. 833.
Chem.-Ztg. vol. 30 part I (1906) p. 431.

Schreib, H.—ON THE QUESTION OF RIVER WATER PURIFICATION.

Comments on Vogel's paper claims priority over Hofer.
Papier-Ztg. vol. 30 (1906) p. 1111.
Z. angew. Chem. vol. 19 (1906) p. 1302.

Hofer, H.—

The author found by experiments with waste sulphite liquor that even at the dilution of 1 part to 100,000 parts of water, formation of algae takes place. This is due to the fermentable sugar, whereas the arabinose, rhammose, and xylose are not injurious.

Allgem. Fischerei Ztg. vol. 31 (1908) p. 71.

Vogel, J. H.—COMMUNICATION ON EFFLUENTS TO THE VEREIN DER ZELLSTOFF-UND PAPIER-CHEMIKER.

This paper deals with (*a*) effluents from paper-mills (*b*) effluents from sulphite-pulp mills (*c*) effluents from sulphate-pulp mills.

(*b*) Effluents from Sulphite-Pulp Mills.

Of all the processes proposed for utilizing the waste liquor none have met with technical or financial success. It is therefore desirable that the proposals of Frank and Lehmann for using the liquor as a cattle food should be investigated and the merits of the proposals decided on.

Purification by precipitating the organic substances with chemicals has not been and probably never will be successful, because precipitation will always be incomplete. Frank's process, which seemed the most useful, has been tried and it has been found that it does not render the liquor totally harmless. The sugar content must first be removed or changed in such a way as to render it harmless, as the presence of sugar increases the growth of algae. Hofer carried out experiments by letting sulphite liquor run into a stream continuously and observed the growth of algae. He found that the fermentable hexoses cause the rapid growth of sphaerotilus algae. He neutralized the sulphite liquor and fermented it with yeast and after driving off the alcohol the liquor was run into streams. No increased growth of algae was observed although the liquor was run in in concentrations of from 1:100 to 1:1000. The algae showed a noticeable tendency to die off; in any case it was impossible by this means to cause the rapid growth of algae.

Experiments with glucose solutions showed the very rapid growth of algae, so in a few days the stream was filled with algae. Solutions of pentoses such as arabinose were without influence on the growth of sphaeroltilus.

When biological treatment of sewage was introduced it was thought that a similar treatment might purify sulphite liquor. When first introduced this biological treatment of sewage was not a success, but with subsequent modifications the treatment was able to render harmless most forms of organic matter, though not that contained in sulphite liquor. Spindler put forward a reason for this in that the organic substances of sulphite liquor are not easily oxidized. Hofer investigated the subject, working on it one year. It had the same chemical composition at the end as at the beginning. The cause of this was that the liquor contains compounds of sulphurous acid, e. g. of lime, dextrose, and ligno-sulphonic acid, which are strongly antiseptic, so that bacteria which can act readily on many organic substances have no effect on sulphite liquor. Hofer remarks that experiments are being carried on with a view to precipitating the sulphurous-acid compounds by means of lime before the biological treatment, but Vogel considers that a very considerable purification must be carried out first, as well as a removal of the lime salts by a process such as Frank's. After this treatment a biological treatment might be successful.

A number of sulphite factories have endeavoured to solve the problem by a high dilution of the liquor. This has been carried out by first adding the wash-waters from the pulp to the liquor and running the same into the stream very slowly. Hofer investigated this subject and found that even at great dilutions if the liquor was run in continuously the algae continued to grow, but if it was discharged intermittently there was a noticeable decrease in the algae. This has been put in practice at several mills but it is too early to have arrived at any definite results.

By allowing the sulphite liquor to stand, the greater part of the content of pulp-fibre sank rapidly to bottom, but the last portion amounting to 4 milligrammes per litre is so fixed that it will not deposit even on standing 8 days. By allowing the liquor to stand the pulp content drops to 10-12 milligrammes which is the limit to be aimed at practically.

Z. angew Chem. vol. 19 (1906) p. 748.

Vogel, J. H.—WASTE SULPHITE LIQUOR.

The sugar content of Mitscherlich liquor is lower than that of Ritter-Kellner liquor. The sugar content is higher in liquors from wood cooked in the fall.

The formation of fungus is not always injurious to the fish and may in many cases be considered as favourable; but the liquor should not contain sulphurous acid. In small rivers the formation of fungus may be so considerable that the entire river-bed is covered, thus preventing the fish from reaching the nutriment of the soil, whereby the spawning places are destroyed. In quiet places in the river the sulphate may be decomposed, forming H_2S which kills the fish.

Purification with copper sulphate is not considered feasible as it will also kill such algae as are necessary for the formation of oxygen and for the absorption of organic matters in the waste water.

Wochbl. Papierfabr. vol. 38 (1907) pp. 881, 958.
Papier-Ztg. vol. 31 (1906) pp. 1278, 1314, 1355.
Z. angew. Chem. vol. 19 (1906) part I p. 750.
Chem. Zentr. (1906) Part I p. 1853.

Konig, J.—POLLUTION OF RIVERS AND UTILIZATION OF WASTE SULPHITE LIQUOR.

Z. angew. Chemie. vol. 19 (1906) part I p. 750.

Verein, Deutscher Zellstoffabrikanten.—DISCUSSION ON THE EFFECT ON FISH OF FUNGI CAUSED BY WASTE SULPHITE LIQUOR.

Report on Meeting held on Feb. 17, 1906.

Schreib, H.—PROCESS FOR PURIFICATION OF EFFLUENTS.

Chem.-Ztg. vol. 31 (1907) pp. 1133, 1157.
Z. angew. Chem. vol. 20 (1907) p. 1986.

Vogel, J. H.—COMMUNICATION ON EFFLUENTS TO THE VEREIN DER ZELLSTOFF—UND PAPIER-CHEMIKER.

(*b*) Sulphite Waste Liquor—Summarizes the comments of Krause and Schreib on his previous paper. Prof. Marston lecturing on the effect of the algae on fish life stated that as a result of many observations there was grounds for considering algae as a useful fish food. It was suggested that copper sulphate might be added to the liquor as a bactericide, but this might be very expensive.

Wochbl. Papierfabr. vol. 38 (1907) pp. 780, 881, 958.
Papier-Ztg. vol. 32 (1907) pp. 961, 1010, 1054, 1098.
Z. angew. Chem. vol. 20 (1907) p. 786.

Kirchner, E.—

Das Papier vol. 2 parts B. and C. Cellulose.
Effluents from Pulp-Mills pp. 200-250, 400-474, 584-587.

Kirchner, E.—

Das Papier vol. 2 pp. 122, 126.

Kolkwitz.—BIOLOGICAL AUTO-PURIFICATION APPLIED TO THE DESTRUCTION OF EFFLUENTS.

Wochbl. Papierfabr. vol. 38 (1907) pp. 1998, 2289.

Oesterreichischer Verein fur Cellulosefabrikation (Austrian Assoc. of Cellulose Manufacturers).—PROCESS FOR MECHANICAL PURIFICATION OF TOTAL EFFLUENTS FROM PULP-MILLS AND PAPER-MILLS.

German Patent 180768.
Papier-Ztg. vol. 32 (1907) part I p. 948.

Weigelt, C.—CHEMICAL AUTO-PURIFICATION OF WATERS.

Archiv fur Hydrobiologie und Planktonkunde Reprint (1907) vol. 2.

Luerssen, A.—WATER POLLUTION BY SULPHITE-CELLULOSE FACTORIES.

The effluent from the plant at Konigsberg was discharged into the River Pregel. It had been observed since 1872 that the river water during the hot months of the year became very offensive, the colour assuming also a deep brown or black tint. A searching inquiry, under the supervision of Prof. Pfleiffer, was made in 1905. It was shown that the organic matters from the cellulose works, especially in warm weather, underwent rapid putrefactive changes which gave rise to the dark colour and the disgusting smell. The decision arrived at was that this effluent must be emptied into the town sewers, and this was allowed on the condition that the liquid underwent a previous treatment with lime or other chemicals and was thoroughly neutralized so as to render the ligno-sulphites harmless. The acid present was not to exceed 0.06 per cent and the water was to be cooled down in large tanks at the factory before admission to the sewers.

Z. Hyg. vol. 58 p. 121.
J. Soc. Chem. Ind. vol. 27 (1908) p. 1220.

POLLUTION OF THE WATERS OF LAKE CHAMPLAIN.

Waters of Lake Champlain to be examined by the New York State Board of Health to ascertain the effect of the discharge into the lake of polluted water from streams on whose banks are located pulp-mills. Large numbers of dead fish are reported, and much slime on rocks that was never seen before the days of the pulp-mill.

Pulp Paper Mag. Can. vol. 1 (1903) p. 126.

Vogel, J. H.—WASTE LIQUORS.

Non-professional opinion frequently fails to distinguish between waste waters from pulp-mills and those from paper-mills. Tests on Mitscherlich and Ritter-Kellner waste lyes show that wood treated in the winter proved richer in saccharine contents than that dealt with in the spring. The percentage by weight of sugar in waste in summer was 0.5 – 0.875; while the percentage in winter was 1.0 – 2.0. Details of a plant to be erected to purify waste lye from soda-pulp mills in such a way that it would be colourless and free from floating substances, are given. Claims that self-cleansing powers of small water-courses should be utilized in proportion to local requirements.

Pulp Paper Mag. Can. vol. 5 (1907) p. 142.

Kolkwitz and Pritzkow, A.—OPINION ON THE EFFLUENTS FROM PULP-MILL AT CZULOW.

Chem. Zentr. (1908) part II p. 2048.
Wochbl. Papierfabr. vol. 39 (1908) p. 332.

Lassar-Cohn.—CONTAMINATION OF RIVER PREGEL.

This is caused by sulphite liquor, it is avoided by turning the sulphite liquor into the canal system.

Papier-Ztg. vol. 33 (1908) part II p. 3379.
Chem.-Ztg. vol. 32 (1908) p. 980.
Chem. Zentr. (1908) part II p. 1545.

Vogel, J. H.—EFFLUENTS FROM PULP-MILLS.

The pollution of rivers by the effluents from sulphite wood-pulp mills may be direct (e.g. by fibres, dissolved organic matters, sulphurous acid) or indirect (e.g. by the growth and subsequent putrefaction of fungi and algae). Of the first class of polluting substances, the cellulose fibres are the most objectionable and the most easily removed. These fibres collect and precipitate impurities from sewage effluents and effluents of other factories and are deposited in the form of putrefying mud at the bottom of the river. On cases of damage due to pollution (e.g. fish poisoning or damage to crops after a flood) the ease with which the fibres are identified causes the responsibility to be thrown on the pulp-mill, even though the fibres are harmless themselves and constitute only a small proportion of the mud. The cost of removing the fibres from the effluents is largely counter-balanced by the value of the recovered product, so that all mills should aim at discharging an effluent containing not more than 40 to 60 milligrammes of suspended fibres per litre, according to the size of the river. The waste liquors themselves if diluted 100 times are perfectly harmless to fish and vegetation, thus no direct damage is likely to ensue from their presence in the river; but the indirect nuisance caused by the growth and putrefaction of fungi may assume grave proportions in a slow-flowing river. The waste liquors at their original concentration are absolutely non-putrescible; the growths are developed by the continuous feeding of the lyes into the channel in a highly dilute form. A mill producing 40 metric tons (44·05 short tons) of cellulose per day will discharge 300 cub. m. (6,600 gallons) of original lye and 780 cub. m. (171,600 gallons) of wash-waters. The lye will very rarely contain 4 grammes of free sulphur dioxide per litre and this will be largely neutralized by the basic constituents of the wash-waters. The best method of preventing growths is to adopt the system of intermittent discharge of large quantities of lye instead of the continuous discharge of small quantities. The lyes in washing should be collected in a reservoir, freed from fibres, and discharged once or twice every 24 hours at such a rate that the total dilution of the original lye amounts to 100 times. The time of discharge might be about 40 minutes but every case requires particular consideration; much depends also on the degree of pollution by putrescible and the deoxidizing effluents from other sources. The author is opposed to the regulation requiring the neutralization of the effluents by lime. A neutral or alkaline condition of lye greatly favours the growth of fungi. It would seem apparently that the "free" sulphurous acid in these lyes is probably in loose combination with sugars and is far less poisonous to fish than pure sulphurous acid. All that is necessary is to insure that the free sulphurous acid does not amount to more than 1 gramme per litre of effluent; the basic matters in the river water will do all that is necessary. In the case of very small water-courses, if the periodical discharge of the effluent be adopted it may be necessary to dilute the lyes in the reservoir before discharging.

Papier-Ztg. vol. 33 (1908) part II pp. 3855. 3890, 3931.
Wochbl. Papierfabr. vol. 40 (1909) pp. 857, 930.
Z. angew. Chem. vol. 22 (1909) p. 49.
J. Soc. Chem. Ind. vol. 28 (1909) p. 158.
Chem. Abs. vol. 3 (1909) p. 1196.
Pulp Paper Mag. Can. vol. 7 (1909) p. 289.

WASTE WATER FROM PULP-MILLS.

Daily amount of waste liquor and wash-water from a 40-ton mill, amount of free sulphurous acid. Recommends intermittent discharge.

World's Paper Trade Rev. vol. 52 (1909) part III p. 36.

Carlson, T.—THE POLLUTION OF THE MONDAL RIVER (SWEDEN).
(See "Composition" p. 12.)

Kolkwitz and Pritzkow.—REPORT ON WASTE LIQUOR FROM KATTOWITZ MILL.

Mitt. Prufungsamt. Wasser u. Abwasser.
Berlin vol. 10 (1909) pp. 1116, 173.
Chem. Abs. vol. 3 (1909) pp. 1661, 1662.

Klason, P.—PURIFICATION OF EFFLUENTS OF SULPHITE MILLS.

For the disposal of the waste lyes from sulphite pulp-mills the correct principle consists in collecting them, with or without the wash-waters, in large reservoirs where they are cooled and aerated. They should then be discharged continuously and regularly into a river of sufficient volume. The main points to be considered are the proportion of the water to the organic matter and the quantity of oxygen dissolved in the water. If, on account of periods of drought, the volume of the river is restricted, large reservoirs should be provided for the storage of the lyes until the weather changes. According to the author's experience, no ill results whatever will result from the continuous discharge into a river which ensures a thousand-fold dilution of the lyes, corresponding to the introduction of 100 grammes of foreign matters per litre. A flow of 1 cub. metre (35·1 cubic feet) per second will deal with the by-products from the manufacture of 7½ metric tons (8·25 short tons) of air-dry cellulose per 24 hours. The average volume of a river may be calculated approximately as 40-60 per cent of the rainfall over the area drained by it. A reservoir capable of storing the lye and wash-waters for a week should be provided, and should be designed with a capacity equal to 70 times the weight of the daily output of cellulose. The lye, diluted and infected with an equal volume of river water, will undergo a fermentation in the course of 7 days storage, which will materially diminish the amount of organic matters ultimately discharged into the river. The self-purification of river-water polluted with sulphite-lyes may be divided into three states. The first is a rapid fermentation of some of the organic matters by organisms nourished by the phosphates and salts extracted from the wood. The oxygen of the water is rapidly consumed and the carbonic acid increases. When the supply of oxygen fails, the organisms respire at the expense of the organic solids in solution and powerful reducing actions supervene; this stage is the most noxious, and since the nitrogenous nutrition is limited it extends over a longer period than the first stage. The final state consists in a slow restoration of the natural condition of the water by the action of chlorophyll-bearing algae under the influence of light. Experiments made by the author showed that water at rest and at a constant temperature dissolves atmospheric oxygen at a slow rate only, but that variations of temperature act in the same way as mechanical agitation and cause a rapid aeration. The injuries to fish caused by sulphite lyes are principally indirect, brought about by the general deoxidation of the water; the resin, and, in soft waters, the free acid also bring about certain objectionable results; while the harm caused by fibres in suspension is practically negligible. Wood contains about 53 per cent of cellulose but yields only about 45 per cent of pulp; the difference may be apportioned as follows: 4 per cent dissolved by chemical hydrolysis; 3 per cent sorted out in cleaning and screening operations; and 1 per cent discharged with the wash-water. Thus the effluents may be estimated to contain, in suspension, about 2 per cent of the cellulose output of the mill; only about one-fourth of this suspended matter consists of thin-walled parenchyma cells which do not settle out on standing.

Wochbl. Papierfabr. vol. 40 (1909) p. 2668.
Papier-Fabr. vol. 7 (1909) pp. 26, 671, 701, 795.
J. Soc. Chem. Ind. vol. 28 (1909) p. 1000.
Papier-Ztg. vol. 35 (1910) p. 2116.
Pulp Paper Mag. Can. vol. 8 (1910) p. 185.
Paper vol. 3 (1911) No. 2 p. 9.

EFFECT OF PAPER-MILL EFFLUENTS ON FISH.

The bad effect is due to fibres and sawdust.

Papier-Fabr. vol. 8 (1910) p. 947.
Z. angew. Chem. (1909) p. 2205.

Schneider, F.—POLLUTION OF STREAMS BY SULPHITE LIQUOR.

The algae which are carried by the pulp-fibres choke up boilers, etc. River water into which sulphite liquor has been discharged will cause a rash on bathers, even though there is not enough liquor present to cause a taste in the water.

Papier-Ztg. vol. 35 (1910) p. 1902.
Z. Hyg. (1907) p. 121.
Papier-Fabr. vol. 7 1909) p. 34.
Z. angew. Chem. vol 22 (1909) p. 655.

COPPER AS PURIFIER FOR WATER.

Moore's invention by which it is claimed that any water is made free from germs in a few hours by addition of small amounts of copper.

Zentr. Wasserbau. vol. 24 (1909) p. 377.

EXPERIMENTS WITH COPPER SULPHATE AS A MEANS OF KILLING ORGANISMS IN PONDS AND RESERVOIRS.

From 37th Annual Report of the Sanitary Board of Massachusetts, Boston, 1906.

Gesund. Ing. vol. 25 (1909) p. 422.

Mackay and Miller.—COST OF TREATMENT OF EFFLUENTS.

J. Soc. Chem. Ind. vol. 28 (1909) p. 1183.

Schall, C.—INNOVATION IN THE PURIFICATION OF EFFLUENTS.

German Patents 194745, 204470, 206743, 206999, 207355, 194744, 197160, 202393, 196390, 194127, 208373, 201052, 197587.

Z. ges. Wasserwirtsch vol. 9 (1909) p. 147.

Pritzkow, A.—THE PRESENT SITUATION OF THE EFFLUENT PROBLEM IN THE SULPHITE MILLS.

Processes of purification and the effects on the waterways. Treatment of waste liquors by natural and artificial biological processes. Elimination by irrigation and evaporation. Utilization of substances contained in the liquor.

Reprint from Vierteljahr. Ger. Med. 3 Folge XL Bol. No. 1 Berlin 1910.
Eng. Record vol. 62 (1910) p. 468.
Chem. Abs. vol. 5 (1911) p. 1144.
Paper vol. 7 (1912) No. 1 p. 23.

Vogel, J. H.—REPORT OF THE ASSOC. OF PULP AND PAPER CHEMISTS (1909) III WATER AND EFFLUENTS.

Part C giving literature on effluents for year 1909.

Papier-Ztg. vol. 35 (1910) p. 1931.

Vogel, J. H.—REPORT ON SULPHITE MILL AT RAGNIT, GERMANY.

The author has reported on the possible pollution of the River Memel by the effluents from a sulphite-pulp mill which it is proposed to erect at Ragnit. The mill would produce 40 metric tons (44 short tons) of cellulose per 24 hours and the amount of effluents per second would consist of 3.47 litres (0.75 gallons) of waste lye; 9.26 litres (2·04 gallons) of cooling, rinsing, and washing waters, and 200 litres (44 gallons) of manufacturing waters. The flow of the river at low water is calculated at 200 cub. m. (7,000 cu. ft.) per second, and the river having numerous curves it is assumed that perfect admixture would be attained at a distance of 8 km. (5 miles) from the works, the dilution of the waste lyes being then 45,000 fold. Under these conditions any injury to the Tilsit waterworks, situated at a distance of 14 km. (8.7 miles), is amply provided against, and destruction of fish and the growth of fungus are considered to be quite out of the question. In addition to the manufacture of wood-pulp it is proposed to bleach 10 tons (11 short tons) of cellulose daily for the manufacture of paper, the bleaching effluents being mixed with the sulphite lyes and assisting their oxidation. The author recommends that the discharge be allowed under the following conditions: The strong waste lyes and the wash-waters used on the pulp for rinsing in the boiler itself, are to be collected in a reservoir of 1,000 cub. m. (35,300 cu. ft.) capacity, from which they are to be mixed after cooling with the constantly flowing clarified waste water from the manufacturing operations, and the diluted effluent discharged into the river. The manufacturing waste water and the used bleaching lyes are only to be admitted to the main effluent pipe after they have been so clarified from fibre that the maximum amount of suspended matter does not exceed 100 milligrams per litre. The main discharge pipe must extend at least 5 metres (16.4 ft.) into the river, and must be provided with perforations for a length of 3 metres (9.84 ft.) at the end in order to avoid discharge of a dense column of polluted liquid.

Papier-Fabr. vol. 9 (1911) p. 438.
J. Soc. Chem. Ind. vol. 30 (1911) p. 532.
Chem. Abs. vol. 5 (1911) p. 2520.

SULPHITE WASTE LIQUOR.

Refers to Mitscherlich's original process for producing cellulose that demanded a dilution of 3,000 times the sewage from his process in order to render it inoffensive.

Three types of waste:—

(1) digester liquor and wash-water;
(2) screen and filter press water from the pulp presses;
(3) condenser water and other water from machine operation.

German conditions: 1·2 gallons of waste liquor from each pound of pulp. In 1908 Germany discharged daily 3,960,000 gallons of waste liquor of which 1,760 tons were solid matter containing 1,230 tons organic matter. Author reviews methods for treatment of waste in streams to destroy growths, etc. Evaporation claimed to be expensive, as a plant in Upper Silesia showed a cost of 82 cents per gallon when evaporating 50,000 gallons of liquor daily.

Pulp Paper Mag. Can. vol. 10 (1912) p. 217.

Kerschaw, G. B.—THE PURIFICATION OF WASTE LIQUORS FROM PAPER-MILLS.

Refers to waste from paper-mills in the manufacture of different papers. The following table was taken from vol. 3 of the 7th Report of the Sewage Disposal Commission:—

PARTS FOR 100,000.

Nature of Sample.	Suspended solids.	Dissolved solids.	Oxygen absorbed.	
			In 3 min.	In 4 hrs.
White papers, crude liquors	204	54	...	20
" "	139	68	4·84	...
Brown papers, crude liquors	290	477	...	39·6
" "	59	106	3·98	...
" "	126	178	...	25·1
Wall papers, crude liquors	185	305	...	27·8
Printing papers, crude liquors	6·2	264	3·92	...
" "	89	157	2·30	...

Pulp Paper Mag. Can. vol. 13 (1915) p. 111.

Reinitzer, B.—CONTAMINATION OF WATER SUPPLIES.

It is stated that by mixing together the waste digestion liquors and the residues from the bleaching process both waste products are rendered innocuous to fish and can be safely discharged into a water-course. The method is said to have worked satisfactorily in practice for a long time.

Papier-Ztg. vol. 36 (1911) pp. 2882, 2913.
Z. angew. Chem. vol. 24 (1911) p. 1851.
J. Soc. Chem. Ind. vol. 30 (1911) p. 1206.
Oesterr. Chem.-Ztg. vol. 15 p. 61.
Chem. Abs. (1912) p. 1480.

Pritzkow, A.—INFLUENCE OF SULPHITE LIQUOR ON RIVER TILSIT.

Mitt. Prufg-Amt. Wasserversorg. u. Abwasserbesseit. (1911) p. 119.
Chem. Zentr. (1911) part II p. 1455.

Rohland, P.—ADSORPTION BY CLAYS, IV (DECOLORIZATION OF WASTE SULPHITE LIQUORS).

The author has shown previously that clays rich in colloids have the power of adsorbing complex animal, vegetable, and artificial colouring matters, but attempts to remove the colouring matter from waste sulphite-cellulose lyes by adsorption with clay failed. The yellowish-brown colouring matter present in these lyes is probably an iron compound, for on adding potassium ferrocyanide the deep greenish-blue colour of Prussian blue makes its appearance after some time. After this preliminary treatment the lyes can be decolorized by means of clay, for the latter adsorbs Prussian blue.

Biochem. Z. vol. 46 (1912) p. 374.
J. Soc. Chem. Ind. vol. 31 (1912) p. 1119.

Wellensick, F.—CLARIFICATION OF EFFLUENTS.

The effluent is treated with an alkaline solution of the humic substance separated from the waste lyes from the manufacture of cellulose from straw or wood, and then with basic or acid salts or other precipitants, e.g. milk of lime or aluminium sulphate.

German Patent 266998 (1913).
J. Soc. Chem. Ind. vol. 33 (1914) p. 39.

Scott, J.—DANGERS AND USES OF WASTE SULPHITE LIQUORS.

The luxuriation of organisms in waters containing waste sulphite liquor seems also to depend on the soil of the river banks and the composition of the water itself.

Paper-Maker Brit. Trade J. vol. 42 (1911) No. 3 p. 401.
Wasser Abwasser vol. 4 (1911) p. 540.

Lassar-Cohn.—PROCESS FOR RENDERING EFFLUENTS FROM SULPHITE MILLS HARMLESS.

The pulp from the digester is pressed before washing and the liquor thereby pressed out is disposed of separately.

German Patent Application 36157 (1913).

Polz, H.—

The author has tried Rohland's Process of Purification with colloid clay and found it impracticable.

Paper-Ztg. vol. 38 (1913) p. 3064.
Wochbl. Papierfabr. vol. 44 (1913) p. 4611.

Rohland, P.—ADSORPTION POWER OF THE HYDROXIDES OF SILICON, ALUMINIUM AND IRON.

The yellowish-brown, vegetable, colouring matter found in sulphite liquor is now adsorbed by the above mentioned hydroxides.

Z. angew. Chem. vol. 80 (1913) p. 174.
Chem. Zentr. (1913) part I p. 1858.

Vogel, J. H.—WASTE WATER FROM SULPHITE MILLS.

The waste liquor should be treated as follows:—

1. The cooking liquor evaporated, mixed with coal, and burned,
2. Remaining waste settled in basins, filtered, and used again,
3. Some of the wastes may be used for irrigation,
4. The white water waste purified by sedimentation in baffled settling basins.

Papier-Ztg. vol. 35 (1911) p. 1547.
Chem. Abs. vol. 6 (1912) p. 803.

Stutzer, A.—PARTIALLY REMOVING COLOURING MATTER FROM THE BACK WATER OF THE SULPHITE-CELLULOSE MILLS.

The liquor is treated with phosphoric acid in the absence of a stronger acid.
German Patent 246658 (1911).
Chem. Abs. vol. 6 (1912) p. 2529.

Rohland, P.—PURIFICATION OF EFFLUENTS WITH COLLOID CLAY.

Answer to Polz's criticism.
Farber-Ztg. vol. 24 (1913) No. 21 p. 401.
Papier-Ztg. vol. 38 (1913) p. 3522.

Techn. Verein fur Zuckerfabrikation.—HUMIN FOR PURIFICATION OF EFFLUENTS.

Humin alone or in mixture with lime has proved favourable in the purification of waste water from the sugar factories. Humin, a brown coal (lignite) extract, has a great adsorption power, encases small particles, and causes them to settle.

Deut. Zuckerind. vol. 36 (1911) p. 243.

Gottstein, L.—THE PROBLEM OF EFFLUENTS.

In a report the author claims that the composition of the liquor is less important than the dilution. Mixing with waste water from cities is often even of sanitary and hygienic effect.

Wochbl. Papierfabr. vol. 43 (1912) p. 4329.

Kolkwitz, R.—THE SULPHURBOGITTUS "THIOPLOCA INGRICA WISLAUCH."

Ber. Botan. Ges. vol. 30 (1912) p. 9 Bornträger, Berlin.

Rohland, P.—THE COLLOID PURIFICATION PROCESS FOR WASTE WATER.

The colouring matter in the sulphite liquor is not absorbed by the colloid clay.
Chem.-Ztg. vol. 37 (1913) p. 754.

INTERMITTENT RELIEVING OF WASTE SULPHITE LIQUOR.

An Austrian sulphite mill of 18 metric tons (19·8 short tons) capacity discharged the liquor diluted by 14 cub. m. (3,080 gallons) water into the river for two hours in every 24 hours. An increase in the formation of fungi in the river was experienced.

Papier-Ztg. vol. 36 (1911) p. 864.

Schlauf, J.—THE SANITARY IMPORTANCE OF THE SULPHITE MANUFACTURE INCLUDING THE BLEACHING WITH CHLORIDE OF LIME.

Mixing of waste liquor with waste bleach liquor.
Paper-Maker Brit. Trade J. vol. 42 (1911) Apr. 1 p. 55.

Tillmann, J.—WATER PURIFICATION AND REMOVAL OF WASTE WATER.

Review of all Processes and Apparatus.
(Ed. W. Knapp, Halle, 1912.)

Walker, W. O.—THE PROBLEM OF THE WASTE LIQUOR FROM SULPHITE PULP MILLS.

A discussion of various methods of utilization. In some countries legislation has been enacted with regard to the disposal of this waste. That condition has not yet arrived in Canada, mainly on account of its large rivers and sparse population.

The waste liquor is usually discharged into rivers and on account of its great volume and high content of organic material it then becomes a source of pollution, renders the water injurious to health, unfit for boiler purposes, and injurious to fish or other life. It causes in many cases the development of algae and in the smaller rivers the stream beds are sometimes completely choked with them. Under certain conditions the sulphite wastes develop large quantities of sulphuretted hydrogen, entailing a rapid loss of dissolved oxygen and the death of all animal and plant life in the stream.

J. Soc. Chem. Ind. vol. 32 (1913) p. 389.
Chem. Eng. vol. 17 (1913) p. 246.

Neresheimer, E.—THE DISPOSAL OF SULPHITE-CELLULOSE WASTE.

The liquor is detrimental less on account of SO_2 and fibres than on account of the large amounts of organic matter. Rivers receiving such wastes show a strong growth of *Sphaerotilus,* large amounts of which die off, resulting in a decided odour nuisance. The continual discharge of the liquor into the river, in high dilution, has proved inefficient. Good results have been obtained by discharging at intervals, as the fungus is very sensitive towards interruption in its food supply. Biologic treatment has not been successful. Evaporation is very expensive.

Die Wasserwirtschaft vol. 6 p. 2.
Wasser Abwasser vol. 7 (1914) p. 408.
Chem. Abs. vol. 8 (1914) p. 1178.

THE PROBLEM OF UTILIZATION OF WASTE WATERS FROM SULPHITE MILLS.

The addition of waste liquor to the city sewer for irrigation fields has proved favourable in Konigsberg, Germany. The emptying of the waste liquor into the harbour has increased the fish nutriment (plankton).

Chem.-Ztg. vol. 38 (1914) pp. 639, 657.
Wochbl. Papierfabr. vol. 46 (1915) p. 144.
Chem. Abs. vol. 8 (1914) p. 3857.

Gottstein, L.—THE PROBLEM OF UTILIZATION OF WASTE WATER FROM THE SULPHITE MILLS.

Correcting several points in the articles by Lassar-Cohn.

Chem.-Ztg. vol. 38 (1914) p. 804.

Splittgerber, A.—DISPOSAL AND UTILIZATION OF CELLULOSE AND PAPER FACTORY WASTE.

A general discussion of the waste liquor problem. Four methods of purification are mentioned; irrigation, artificial biologic treatment, infiltration, and evaporation.

Chem. Abs. vol. 9 (1915) p. 376.
Wasser u. Gas. (1914) pp. 243-5, 268-70, 290-3, 313-6.
Wasser Abwasser vol 7 (1914) p. 24.

Hofer, H.—WASTE SULPHITE LIQUOR, GROUND-WOOD PULP, AND CELLULOSE AS NUTRIMENT IN FISH PONDS.

Waste liquor containing no free SO_2 wood-pulp and cellulose, which contains sugar or yields sugar on fermentation, have been found beneficial to fish life and growth and to the growth of plankton upon which the fish feed.

Allgem. Fischerei. Ztg. (1915) Nos. 20,21.
Papier-Ztg. vol. 41 (1916) p. 1.
Chem. Abs. vol. 10 (1916) p. 1432.

Schmidt-Nielsen, S.—THE POLLUTION OF DRAMMENS RIVER (NORWAY) CAUSED BY PULP-MILLS AND PAPER-MILLS, 1911 AND 1912.

Biological and chemical investigations.

An investigation of the fibre losses from some 20 mills proved that these varied for the various mills between 1 and 10 per cent of the dry production, depending on the technical arrangements for recovery. The average length of the fibres were from 0·6 to 1·7 millimetres and several fibres, especially from the chemical pulp-mills and the paper-mills, reached a length of 3-4-5 millimetres. The losses do not consist chiefly of the less valuable parenchyma cells but to a great extent of good tracheids. At a certain point the river receives from the mills not less than 13,000 kg. (28,600 lb.) dry fibres and 200,000 kg. (440,000 lb.) dissolved organic substances in 24 hours, and in addition to this impurities from the logging. The reasons why the troubles caused by this pollution are not more pronounced are the facts that the mills are distributed over a long distance and that the quantity of water in the river is large enough for an effective dilution. The water is also very effectively aerated in the many waterfalls along the river.

The river-bed is covered with a grey layer of algae which holds very strongly together, whereas the algae usually present in rivers is, as a rule, brown or greenish-brown and very loose. The algae grows rapidly in the presence of permanent nutriment in a low concentration from the waste liquors. Also, fibres are absorbed which strengthen the algae layers and contain nutriment for organisms.

No investigations have been made to determine the effect of the normal algae layer upon the breeding of the salmon spawn, but if the algae layer forms the basis for fungus and bacteria growth the salmon spawn no doubt are damaged.

Papir J. vol. 4 (1916) No. 2 pp. 17, 196.

Graetz, B.—PURIFYING SULPHITE BACK-WATER.

The sulphite liquor is treated with fuel ash.

Swiss Patent 73107 (1916).
Danish Patent 21889 (1917).
Chem. Abs. vol. 11 (1917) pp. 100, 2153.
Pulp Paper Mag. Can. vol. 15 (1917) p. 741.

Hoskins, W.—SEPARATING SUSPENDED PULP FROM SULPHITE EFFLUENTS.

The waste liquor is passed over a layer of limestone. The CO_2 generated by the action of the acid in the solution upon the $CaCO_3$ carries the pulp to the surface, and it is skimmed off and recovered.

United States Patent 1226333 (1917).
Chem. Abs. vol. 11 (1917) p. 2153.
Pulp Paper Mag. Can. vol. 15 (1917) p. 741.

BINDING MATERIAL

When waste sulphite liquor is concentrated to a thick liquid or to dryness a tar-like product is obtained which consists chiefly of compounds of lignin-sulphonic acid in admixture with sugars, and which is suitable as a binding material for powdered substances. The most important operation in the manufacture of a binder from the waste liquor is, therefore, the evaporation, but it is also often recommended in the numerous patents to purify the liquor before the evaporation by removing certain products which are not desired in the final binding material.

The binding power may be increased or other qualities of the ultimate products may be obtained by the addition of certain substances to the liquor. In some cases when it is desired to remove part of the calcium from the solution, sulphuric acid or a sulphate is added to the crude liquor, in other cases the liquor is neutralized with lime before evaporation. Instead of preparing the binder for briquetting separately it has also been proposed to mix the liquor with the briquetting material and other substances directly, as in the German Patents 246289 and 252439, according to which sulphuric acid or an acid compound is added to a mixture of sulphite liquor and briquetting material, with or without the addition of aldehydes. The mixture is heated to the point of gelatinization, which can be accelerated by adding such substances as tar, tar-products, asphalt, etc. Afterwards the briquettes are dried below 200°C.

Among the many uses for which the binder from sulphite liquor has been recommended are binding material for briquetting powdered fuel (such as coal, peat, sawdust, etc.), blast furnace dust, and fine pyrites. The binder is also used in foundries for making sand cores and for binding dust on roads.

It has been pointed out as a drawback in the use of concentrated waste sulphite liquor as a binding material for briquetting powdered fuel that it is hygroscopic and soluble in water and, therefore, the briquettes are not weather resistant. Many methods for the elimination of this disadvantage have been patented. It has been recommended to heat the briquettes to a high temperature in order to carbonize the binder or to add to the liquor compounds of chromium and finally aluminum sulphate. Pollacsek has patented a process whereby the briquettes are immersed in a mixture obtained by heating crude petroleum oil, containing paraffin or ozokerite substances with bitumen and phenols, to the boiling point with strong aeration, until a mixture is obtained which solidifies on cooling. Favourable results have been reported by iron works regarding the use of waste sulphite liquor for briquetting coke dust and fine ore. According to Mathesius the reduction of iron ore is more favourable with briquettes, and a great saving in coke and an increased production has been experienced.

In late years a product called "Zellpech" or "cell-pitch" has been manufactured and has occasioned considerable interesting discussion. The product is obtained by neutralizing the cooled liquor in wooden vats and filtering it through coke, whereupon the filtrate is concentrated by evaporation to a density of 35° Bé. and used in this form, or is evaporated to dryness and made into blocks. This pitch contains 10 per cent moisture and represents 10 per cent of the original liquor. It has the appearance of a black, opaque rosin and is soluble in water. For the production of one ton of "cell-pitch" one ton of coal is required. Its heat value is 3,166 calories (5,700 B.T.U.). The price of 10-12 dollars (in 1912) per ton is very close to that of tar. But for binding fine coal only 5 per cent of this pitch is required, whereas 7-10 per cent of tar pitch is used. Cell-pitch is also used for impregnating sail-cloth and ropes, and as a filling material. Blast furnace dust containing about 40 per cent iron may be mixed with ground cell-pitch, the proportion of pitch being 4-5 per cent. The mixture is heated with superheated steam at 350°-420° C. and pressed into bricks. These bricks do not lose their shape in the furnace at a temperature of 1,600° C.

In Europe as well as in America waste sulphite liquor concentrated and neutralized has been used as a road-binder with apparent success. The United States Department of Agriculture made extensive experiments with waste sulphite liquor, with the result that concentrated liquor of a specific gravity of 1.13 may be classified as a temporary or semi-permanent dust preventive and road-binder. Half a gallon per square yard was effective for a period of 6 weeks. The cost including labour and material was estimated to be $0.0355 per square yard. The results of comparative tests at Queen's University, Kingston, Ontario, were in favour of using concentrated (4:1) waste sulphite liquor instead of road oil. The road oil was washed away at the end of 4 months, whereas the roads treated with waste liquor directly or after previous treatment with oil still presented a hard surface at the end of that period. It has been suggested that the binding and water-resisting qualities be improved by emulsifying the liquor with mineral oil.

Nettl, A. S.—PROCESS FOR TRANSFORMING THE WASTE LIQUORS FROM THE MANUFACTURE OF SULPHITE CELLULOSE INTO SUBSTANCES MADE AVAILABLE FOR INDUSTRY.

Austrian Privilegium 1576 (1888).
(See " Gums, Adhesives and Sizing Material " p. 68.)

Ullmann, H.—PROCESS FOR UTILIZING SULPHITE LIQUOR AS A BINDING MATERIAL.

The liquor, evaporated at least one-half, is treated with alkaline carbonates by which the dissolved organic substances are precipitated. It is proposed to use the precipitate as a binding material for briquetting wood, coke, and coal.

Austrian Privilegium 3043 (1890).

Mitscherlich ,A.—PROCESS FOR THE PRODUCTION OF TANNING MATERIALS, ADHESIVES, AND OTHER SUBSTANCES FROM WASTE SULPHITE LIQUORS BY OSMOSIS.

German Patent 72161 (1891).
English Patent 12927 (1893).
(See " Tanning Materials " p. 78.)

Mitscherlich, A.—PROCESS FOR PREPARING ADHESIVES, BINDING AND CONCENTRATING MATERIALS FROM WASTE SULPHITE LIQUORS.

The liquor is directly neutralized with milk of lime without osmosis, then evaporated to a specific gravity of 1·2 and mixed while hot with one-fourth of its volume of a paste of lime of specific gravity 1·2 until the lime is absorbed and a thick, transparent substance is formed. This organic lime compound should be used for preparing coal briquettes, for binding powder substances, and for concentrating purposes.

German Patent 72362 (1891).
Ber. vol. 27 (1894) p. 221.
Papier-Ztg. vol. 19 (1894) p. 272.

Jürgensen, F., Niesz, Fr., Gümbel, G.—ADHESIVES LIKE THAT PRODUCED BY PATENT 72386 ESPECIALLY FOR COATING CONTAINERS FOR PETROLEUM, ETC.

German Patent 73718 (1892).
(See " Gums, Adhesives, and Sizing Materials " p. 68.)

Griffin, M. L.—PROCESS FOR PRODUCING A PLASTER.

Glue is dissolved in hot, waste sulphite liquor and the mixture when cooled is mixed with gypsum, fibrous material, sand or marble. The plaster has a low heat conductivity and is suitable for plastering purposes.

German Patent 69874 (1892).
Ber. vol. 26 (1893) p. 905.

COAL BRIQUETTES MADE WITH WASTE SULPHITE LIQUOR.

The remaining adhesive product from the evaporation of waste liquor has been used since 1893 in an iron works in Hungary as a binding material in the manufacture of briquettes from charcoal dust.

Hofmann, C., Handbuch der Papierfabrikation 2nd edition (1897) p. 1620.
Papier-Ztg. vol. 21 (1896) p. 1183, vol. 22 (1897) p. 3647.
J. Soc. Chem. Ind. vol. 15 (1896) p. 579.

Pollacsek, E.—TREATMENT OF WASTE LIQUOR FROM THE SULPHITE PROCESS.

The liquors, not previously purified, are mixed at ordinary temperature with fine coal, peat, or similar fuel with the addition of lime and kagnesite in the proportion of 1 part waste liquor, 5 parts coal or other material, 1 per cent of the mixture of lime, and ½ per cent of magnesia.

Austrian Privilegium 985 (1898).

Schild, H.—SULPHITE WASTE LIQUOR AS A BRIQUETTING MATERIAL.

According to German Patent 111757, coal for cooking purposes is preferably mixed with partially evaporated sulphite liquor. The amount to be added to each grade of coal must be found by experiment. Ten per cent of the weight of coal is usually used. The ash is thereby increased by about 0·5 per cent.

Papier-Ztg. vol. 25 (1900) part I p. 1725 part II pp. 1125, 2456.
Jahrb. Chem. Techn. (1900) Part I, p. 15.

Trainer, E.—PROCESS FOR PREPARATION OF A BRIQUETTING MATERIAL.

The liquor in a syrupy state has previously been used as a briquetting material. The hard brittle substance obtained from the evaporation of the liquor is now mixed with the coal dust, the mixture heated, and subjected to pressure.

German Patent 136322 (1900).
Chem. Zentr. (1902) p. 410.
Papier-Ztg. vol. 27 (1902) part II p. 3478.

Trainer, E.—PREPARATION OF A BRIQUETTING MATERIAL FROM CARBOHYDRATES, (ALBUMINOIDS, RESINS, ETC.)

The above named substances are boiled under pressure with acid sulphites, and the resulting liquid is evaporated to dryness. The dry mass can be used as a briquetting agent.

German Patent 140542 (1900).
Jahrb. Chem. Techn. (1903) p. 162.

Trainer, E.—PREPARATION OF A BRIQUETTING MATERIAL.

Tar, resin or wax, etc., may be added to the liquor before evaporating.

German Patent 140862 (1900) (addition to Ger. Patent 136322).
Papier-Ztg. vol. 28 (1903) part II p. 1942.
Jahrb. Chem. Techn. (1903) part I p. 16.
Wochbl. Papierfabr. vol. 34 (1903) p. 2658.

Trainer, E.—PROCESS FOR PREPARATION OF WATER-RESISTANT BRIQUETTES WITH WASTE LIQUORS.

The mixture of binding material and fuel is exposed to heat at not less than 120° C.

German Patent 144819 (1902).
Papier-Ztg. vol. 28 (1903) pp. 86, 3086.

PROCESS FOR UTILIZATION OF WASTE LIQUORS FROM THE SULPHITE PULP-MILLS.

Discussion of the Trainer process, German Patent 140862 (1900).

Papier-Fabr. vol 1 (1903) p. 419.

Partington, E.—UTILIZATION OF SULPHITE LIQUOR.

The author has used sulphite liquor as a binder for street dust.

Papier-Ztg. vol. 29 (1904) part II p. 2686.

Trainer, E.—PREPARATION OF A BRIQUETTING MATERIAL.

The sulphite liquor is concentrated to a point such that, without mechanical means, a powdery substance is obtained.

German Patent 161675 (1903).
Jahrb. Chem. Techn. (1905) part I p. 19.
Papier-Ztg. vol. 30 (1905) part II p. 2582.

UTILIZATION OF WASTE-SULPHITE LIQUOR.

Mechanical disintegration after cooling of the binding material obtained by Trainer's method.

Papier-Fabr. vol. 3 (1905) p. 1557.

Gewerkschaft Eduard.—ZELLPECH (CELL-PITCH).

Manufacture, use, and sale of binding materials for briquettes. Erecting and operating of briquetting plants. Solid and liquid binding materials.

Wortschutzregister 13 93426 G. 6103 (1905).

Elb, M.—BRIQUETTING MATERIAL FROM SULPHITE LIQUOR.

The adhesive substance prepared according to German Patent 166947 (1905) is now used for a briquetting material. By heating the briquettes they may be made insoluble in water.

German Patent 173686 (1905).
Papier-Ztg. vol. 31 (1906) part II p. 3180.
Chem. Zentr. (1906) part II p. 924.
(See "Gums, Adhesives, and Sizing Materials" p. 68.)

Tavernier, A. E. and Oulman C.—UTILIZATION OF WASTE CELLULOSE LYES.

Waste cellulose lyes from paper manufacture are treated with sulphuric acid and concentrated to a syrupy consistency, then well mixed with about 20 parts of the previously ground and sifted fuel. The mixture is heated for 10 minutes with direct steam, then formed into a paste and pressed in a briquette press under pressure of 220 kilogrammes per sq. cm. (3,130 lb. per sq. in.) The briquettes are dried in a chamber built of bricks and covered with red lead. Vapours of hydrochloric acid are passed through the chamber. By the action of the acid the cellulose is transformed into carbon and thus made insoluble. The hydrochloric acid vapours are received in water and used again.

French Patent 359239 (1905).
German Patent 186775 (1906).
Wochbl. Papierfabr. vol. 38 (1907) p. 3048.
Chem. Zentr. (1907) part II p. 1276.
J. Soc. Chem. Ind. vol. 35 (1906) p. 365.

Sachs.-Bankges, Quellmalz and Co.—PROCESS FOR MANUFACTURING WEATHER-RESISTANT BRIQUETTES WITH WATER-SOLUBLE BINDING MATERIAL.

The finished briquettes are heated to a temperature that will carbonize or coke the binding material without changing the briquetting material appreciably.

German Patent 158497 (1906).

Sachs.-Bankges, Quellmalz & Co.—PROCESS FOR MANUFACTURING BRIQUETTES.

In using gas coal it is heated separately before briquetting at a temperature a little above that required for the coking of the binding material, so that the volatile gases may be removed.

German Patent 186652 (1907).
Addition to German Patent 158497 (1906).

Sachs.-Bankges, Quellmalz & Co.—PROCESS FOR INCREASING THE WEATHER-RESISTING QUALITIES OF BRIQUETTES.

Chromium compounds and, finally, aluminium sulphate are added to the waste sulphite liquor.

UTILIZATION OF WASTE SULPHITE LIQUOR.

The use of waste liquor for making cores according to patents by A. Bastian and M. Elb. One thousand kilogrammes (2,204 lb.) of sand requires 5 kilogrammes (11 lb.) of concentrated liquor.

Papier-Fabr. vol. 4 (1906) p. 3128.

Wagner, B.—PREPARATION OF A BRIQUETTING MATERIAL.

The best temperature of the liquor for briquetting is 60°, with the substance to be briquetted at 140°. The whole mixture is then compressed at a temperature of 100°.

German Patent 188428 (1906).
Papier-Ztg. vol. 32 (1907) part II p. 3356.
Wochbl. Papierfabr. vol. 38 (1907) p. 3579.
Jahrb. Chem. Techn. (1907) part I p. 10.

Kumpfmiller, A.—PROCESS FOR BRIQUETTING BY MEANS OF SULPHITE LIQUOR.

Sawdust is mixed with unconcentrated sulphite liquor, dried and shaped under heavy pressure.

German Patent 189177 (1904).
(See German Patent 195286, 199279, 176722, Presses for bulky substance.)
Papier-Ztg. vol. 32 (1907) part II p. 3356.
Chem. Zentr. (1908) p. 1118.
Wochbl. Papierfabr. vol. 38 (1907) p. 3049.
Jahrb. Chem. Techn. (1907) part I p. 8.

Gewerkschaft, Eduard.—PROCESS FOR ALLAYING DUST.

1. Streets are sprinkled with sulphite liquor after the liquor has been heated with acids.
2. Same as (1) except that the sulphite liquor is treated with aldehydes instead of acids.
3. As in (1) but the liquor after treatment as in (1) or (2) is mixed with tar.

German Patent 200210 (1907).
Chem.-Ztg. vol. 32 (1908) Rep. p. 478.
Papier-Ztg. vol. 33 (1908) part II p. 2014.

Kumpfmiller, A.—PROCESS FOR PURIFICATION OF WASTE SULPHITE LIQUOR.

Austrian Patent 40657 (1906).
(See " Miscellaneous " p. 168.)

Gewerkschaft, Eduard.—BINDING MATERIAL IN FORM OF POWDER MANUFACTURED FROM WASTE LIQUOR.

Swedish Patent 23464 (1906).
Chem.-Ztg. vol. 32 (1908) Rep. p. 82.

Robeson, J. S.—PYRITES BRIQUETTES.

Non-hygroscopic briquettes are made from fine pyrites and highly concentrated waste liquor. The briquettes give the same yield of SO_2 as the pyrites.

United States Patent 1013614 (1912).
German Patent 238119 (1907).
Papier-Ztg. vol. 38 (1913) p. 1221.
Chem. Abs. vol. 6 (1912) pp. 591, 1592.

Sembritzki, W.—CELL-PITCH FROM WASTE LIQUOR.

At Walsum on the Rhine the hot sulphite liquors discharged from the digesters flow through cooled lead pipes into an acid-proof reservoir. Thence the liquor is pumped into wooden vats in which it is neutralized with lime; it is filtered through coke, heated to about 97°C., by passage through an economizer, and concentrated to a density of 35° Bé., in an evaporator. Much of this syrup is exported to England for use as a binder for moulds in foundries. The rest is evaporated to dryness by means of revolving steam-heated drums, from which the pitch, containing 90 per cent of dry substance, is moulded into blocks of about 1 cwt. (112 lb.) each. The pitch has the appearance of black, opaque rosin, but is readily soluble in water. The yield of pitch is 10 per cent of the liquors, and a ton of coal is required to make a ton of pitch. This cell-pitch is used for briquetting blast-furnace dust, hitherto a waste product, although containing about 40 per cent of iron. The dry dust is mixed with ground cell-pitch and the mixture is treated in a mixer with superheated steam at a temperature of 350° - 420°C. The mixture, which must not be so moist as to become sticky, is then pressed into bricks weighing about 3 kilogrammes (6·6 lb.); the proportion of pitch is 4-5 per cent. The bricks do not lose their shape in the blast-furnace at a temperature of 1600°C. since the pitch does not volatilize at a high temperature, but only cokes. The price of the pitch is 50 marks per metric ton ($10.88 per short ton). Cell-pitch may also be used for briquetting coal-dust; it is also employed as a filling material, for the preparation of a cheap, black dyestuff for cotton fabrics, and for impregnating sail-cloths and ropes. The crude waste liquors are valued at 5 pfennigs per metric ton ($0.01 per short ton) and the author states that a profitable means of disposing of these wastes has not been found.

Wochbl. Papierfabr. vol. 39 (1908) pp. 658,2866.
Chem.-Ztg. vol. 32 (1908) Rep. p. 221.
J. Soc. Chem. Ind. vol. 27 (1908) pp. 466, 915
Papier-Ztg. vol. 33 (1908) p. 872.
Chem. Abs. vol. 2 (1908) pp. 484, 1885, 3463.
Pulp Paper Mag. Can. vol. 6 (1908) p. 257.

Kayser, H.—EVAPORATION OF WASTE SULPHITE LIQUOR.

The author doubts that the cell-pitch from all mills can be utilized, and announces a new method for separating water from the residue of waste liquors.

Wochbl. Papierfabr. vol. 39 (1908) p. 2201.

Knoesel, Th.—PREPARATION OF CELL-PITCH.

Discussion of Sembritzki's statements. Effect of the lime content of cell-pitch in the blast furnace.

Wochbl. Papierfabr. vol. 39 (1908) p. 3276, vol. 40 (1909) p. 4049.
Chem. Abs. vol. 3 (1909) pp. 484, 1083.

Gewerkschaft, Eduard.—PROCESS FOR BRIQUETTING WITH CONCENTRATED WASTE SULPHITE LIQUOR.

To the mixture of liquor and briquetting material and acid (10-15 per cent H_2SO_4) or an acid compound is added, and this mixture heated to gelatinization. The briquettes are then dried below 200°C. Besides the acid, aldehydes may also be added.

German Patent 246289 (1908).

Gewerkschaft, Eduard.—PROCESS FOR BRIQUETTING.

The gelatinization is accelerated by adding to the liquor substances such as tar, tar-products or asphalt.

German Patent 252439 (1908) (addition to German Patent 246289 (1908).
Z. angew Chem. vol. 25 (1912) p. 2359.
Chem. Abs. vol. 7 (1913) p. 416.

WASTE SULPHITE LIQUOR AS ROAD-BINDER.

Concentrated waste liquor is valued at 12 marks, per 1000 kilogrammes ($2.60 per short ton) in Silesia. Rogers Pulp-mills in Au Sable Forks, N.Y., produce road-binder and obtain 15 cents a gallon.

Paper Trade J. vol. 49 (1909) p. 44.
Papier-Ztg. vol. 35 (1910) p. 1589.

TRANSPORTATION OF CONCENTRATED WASTE LIQUOR IN TANK CARS.

Z. angew. Chem. vol. 23 (1910) p. 1216.
Papier-Ztg. vol. 35 (1910) pp. 451, 2077.
Papier-Fabr. vol. 8 (1910) p. 820.

Opitz and Kayser.—CELL-PITCH FROM WASTE LIQUORS.

Evaporation by use of superheated water under pressure.

Wochbl. Papierfabr. vol. 39 (1908) p. 1299.

Müller, M.—EVAPORATION OF WASTE LIQUORS.

Discussion of Opitz's and Kayser's statements

Wochbl. Papierfabr. vol. 39 (1908) p. 1484.

WASTE SULPHITE LIQUOR AS ROAD-BINDER.

Experiments in Breslau and Czulow.

Papier-Ztg. vol. 34 (1909) part II p. 4018.
Papier-Fabr. vol. 7 (1909) pp. 143, 172.

Badermann, G.—GERMAN RAILWAY TRANSPORTATION OF SULPHITE LIQUOR.

The German railway authorities have decided to recommend that concentrated waste lyes from the manufacture of sulphite wood-pulp be included among the substances suitable for transportation in tank cars. This concession has been made at the instance of the Pionier factory at Walsum on the Rhine which is producing a solid form of these lyes under the name of "Zellpech," as well as a thick, syrupy product which is not so concentrated and which at present is transported in iron drums. The value of the fluid is only M.2-2·5 per 100 kilogrammes ($0.22-$0.27 per 100 lb.) and whereas the Walsum mill in 1908 dispatched 1,830 metric tons of solid "Zellpech" it has only disposed of 150 metric tons of the fluid. On the other hand, the fluid material is more suitable for use in the briquette industry than the solid, and it is hoped that increased transportation facilities will lead to its extended employment. The Pionier factory expects to dispatch 35 metric tons daily of this fluid to a briquette mill in the current year.

Z. angew. Chem. vol. 23 (1910) p. 1216.
J. Soc. Chem. Ind. vol. 29 (1910) p. 874.

Robeson, J. S,—MOULDED ARTICLES, AS BRIQUETTES, CORES OR MOULDS, FORMED FROM SAND WITH A BINDER OF CONCENTRATED WASTE SULPHITE LIQUOR AND WITH A COATING OF THE LATTER.

United States Patents 947101 (1909), 947128 (1910).
Chem. Abs. vol. 4 (1910) p. 652.

Schorr, R.—BINDING MATERIAL FROM WASTE SULPHITE LIQUOR.

Discussion of process for preparation of binder.
Eng. Mining J. vol. 88 (1910) p. 451.
Chem. Abs. vol. 4 (1910) p. 1369.

Weldert, R.—BINDING OF DUST ON ROADS WITH WASTE WATERS.

Gesund. Ing. vol. 32 (1909) p. 723.
Chem.-Ztg. vol. 33 (1909) Rep. p. 617.
Papier-Ztg. vol. 35 (1910) p. 300.

Tavernier, A. E. and Oulman, C.—MANUFACTURE OF BRIQUETTES BY MEANS OF "CELLULIDE".

The binding material "cellulide" is prepared by concentrating the lyes obtained in treating wood for the manufacture of paper pulp, the lyes being first mixed with sulphuric acid. The solid substance, in the form of thin sheets, is mixed with anthracite dust, the mass is treated in a vessel heated by steam, and the pasty mass thus produced is briquetted. The briquettes are stacked on trolleys and passed through a special furnace where they are heated to 300°C., in the absence of air, in order to render them insoluble, smokeless, and odourless. This furnace comprises three compartments separated by sliding doors. In the first compartment the temperature is raised to 100°C., and in the second to 300°C., and in the third compartment the briquettes are cooled to about 120°C. by introducing steam or by a water spray.

French Patent 413152 (1910).
J. Soc. Chem. Ind. vol. 29 (1910) p. 1095.

Trainer, E. and Haage, W.—MANUFACTURE OF BRIQUETTES.

Weather-proof briquettes are made by using, as an agglomerating material, waste sulphite pulp liquor practically freed from soluble calcium compounds and mixed with a chromium compound with or without the addition of aluminium sulphate.

United States Patent 969504 (1910).
English Patent 6631 (1910).
J. Soc. Schem. Ind. vol. 29 (1910) p. 1148, vol. 30 (1911) p. 410

Trainer, E.—MANUFACTURE OF FUEL BRIQUETTES.

The process consists in adding an aldehyde and a substance having an acid reaction to the concentrated waste lye from the sulphite-cellulose process, heating the mixture until it gelatinizes, adding the mass to the fuel, and drying by heat.

United States Patent 974001 (1910).
J. Soc. Chem. Ind. vol. 29 (1910) p. 1365.

WASTE SULPHITE LIQUOR FOR ROAD MAKING.

Waste sulphite liquor, which is produced in the manufacture of wood-pulp, has been the subject of extensive experiments by the United States Department of Agriculture. The material proved to be of little value in single treatment of dusty roads, but the concentrated material became a semi-permanent dust preventive and road-binder. In localities where the crude liquor is produced, frequent application for an extended period might prove to be valuable in making permanent roads.

Oil, Paint Drug. Rep. (1910) July 18.
J. Soc. Chem. Ind. vol. 29 (1910) p. 947.

Nicolle, A.—AGGLOMERATION OF PULVERULENT MATERIALS.

The residual liquors of the sulphite-pulp process contain bodies, chiefly calcium lignosulphonate, which are useful as agglomerates. The chief objection to their use is that the briquettes made with such residue will not stand exposure to the atmosphere without disintegrating. It has been found that salts of chromium, iron, cerium, and other metals of that group have the property of rendering these lignosulphonate bodies insoluble. Formerly the waste liquors were evaporated to dryness at a considerable cost, but according to the process named this is not necessary. The waste liquor is evaporated to a syrupy consistency only, and from 10 to 25 per cent of one of the above mentioned salts is added. Briquettes formed with this mixture are said to be able to resist atmospheric exposure. If preferred, the briquettes may be first made with the concentrated liquor and then afterwards passed through a bath containing about ten per cent of one of the salts alluded to, dissolved in water.

French Patent 425991 (1910).
J. Soc. Chem. Ind. vol. 30 (1911) p. 951.

WASTE SULPHITE LIQUOR AND PREVENTION OF DUST.

Report on experiments with waste sulphite liquor as a road-binder. Concentrated and afterwards diluted liquor gave the best results.

Paper (1910) No. 2 p. 11.

DUST-BINDER.

Good results are obtained in Hartha by using waste sulphite liquor as a dust-binder on roads.

Papier-Ztg. vol. 36 (1911) p. 2562.

BISULPHITE PITCH.

Reports on the use of cell-pitch as a briquetting material for coal in the mill. Cell-pitch has only proved satisfactory in a moderate addition to the ordinary binding material for briquettes.

Mon. Pap. vol. 46 (1910) p. 129.
Papier-Ztg. vol. 35 (1910) p. 2940.

CELL-PITCH AS BINDER FOR COKE AND BRIQUETTES.

The briquettes made with tar-pitch as binding material are not transportable and turn soft in the furnace. The briquettes made with cell-pitch have turned out well except with regard to their resistance to weather. They are of about the same value as the tar briquettes with regard to effect and evaporation. The cost of steam is less favourable, due to the higher price of the cell-pitch.

Papier-fabr. vol. 8 (1910) p. 1160.

Franke, G.—BRIQUETTING WITH CELL-PITCH.

Textbook on the Manufacture of Briquettes (F. Enke, Stuttgart, 1910), volume 2, p. 72: Discussion of briquetting with cell-pitch. Previous treatment and after treatment in order to obtain weather-resistant briquettes. Various kinds of briquettes for fuel. Estimation of cost.

Haage, W.—PROCESS FOR RENDERING BRIQUETTES MADE WITH WASTE LIQUOR AS BINDING MATERIAL WEATHER-RESISTANT.

Anhydrous chromic acid or soluble chromium compounds are added to the liquor. The lime compounds may be previously precipitated (e.g. with H_2SO_4) from the liquor in order to prevent reaction between a portion of their compounds and the chromium compounds.

German Patent 228721 (1908).
Chem. Zentr. (1911) part II p. 1789.
Papier-Ztg. vol. 36 (1911) p. 67.
Chem. Abs. vol. 5 (1911) p. 2177.

Scott, J.—DANGERS AND USES OF WASTE SULPHITE LIQUOR.

In the United States the concentrated liquor has proved favourable as a road-binder.

Paper-Maker Brit. Trade J. vol. 42 (1911) No. 3 p. 401.
Wasser Abwasser vol. 4 (1911) p. 540.

WASTE SULPHITE LIQUOR FOR DUST PREVENTION.

Experiments conducted by the Office of Public Roads, United States Department of Agriculture, indicated that the application of a sulphite solution of specific gravity 1·13 at a rate of 0·5 gallons (0·417 Imperial gallons) per square yard was effective for a period of about 6 weeks. The cost including labour and material was estimated at $0.0355 per square yard. Nothing was gained by employing a more concentrated solution. The sulphite liquor must be classified as a temporary or semi-permanent dust preventive and road-binder.

Eng. Record vol. 62 (1910) p. 251.
Chem. Abs. vol. 5 (1911) p. 981.

Little, A. D.—PROGRESS IN THE MANUFACTURE OF SULPHITE PULP IN 1906.

(See " General " p. 185.)

Richter, Aug.—MANUFACTURE OF BRIQUETTES.

Oils with high carbon-contents, such as tar oils, are added to the waste liquor, and the briquettes heated to 250°-270° C. Example: Five parts creosote oil, 10 parts concentrated sulphite liquor of 36°Bé., 2 parts sulphuric acid of 60° Bé., and 80 parts fine coal.

German Patent Appl. R. 31311 (1910).

USE FOR SULPHITE LIQUOR (CELL-PITCH).

Description of preparation at a German mill.

Neutralized by lime, evaporation in sextriple effect Kestner evaporator to thick fluid, converted into solid pitch by drums heated by steam which dip below the surface of the liquid. Ten pounds of waste lye per pound of dry pitch. Soluble in water; has appearance of black opaque resin. Can be used as a binder for blast-furnace dust, breeze, small coke, and fine ores. Briquettes rendered waterproof by passing them through an emulsion of water and bitumen, and then dried. This process has been selected for the state collieries by the Hungarian Government.

Pulp Paper Mag. Can. vol. 10 (1912) p. 247.

Richter, A.—PROCESS OF PREPARING BRIQUETTES, USING WASTE SULPHITE LIQUOR; TREATED WITH SULPHURIC ACID AS BINDING MATERIAL.

Coal dust or other carbonaceous substances are mixed with a binding agent composed of waste sulphite liquor, sulphuric acid, and tar oils or similar oils, briquetted and heated to 250°-270°C. to carbonize the binding agent. Instead of sulphuric acid its acid compounds such as aluminum sulphate, alum, etc., in solution may be added to the liquor.

German Patent 275832 (1910).
Papier-Ztg. vol. 39 (1914) p. 2021.
J. Soc. Chem. Ind. vol. 33 (1914) p. 1043.

Gunther, W.—SEPARATION OF LIME AS SULPHATE FROM SULPHITE LIQUORS TO BE USED IN BRIQUETTING.

The lime is precipitated by means of the sulphates of those metals which form the chief constituents of the ore to be briquetted or to be reduced by briquetted fuel.

German Patent 255853 (1910).
J. Soc. Chem. Ind. vol. 32 (1913) p. 284.
Chem. Abs. vol. 7 (1913) p. 1869.

Albert, K. and Behrend, L.—PROCESS FOR PREPARATION OF PERFECT EMULSION OF ASPHALT, TARS, OILS, CARBOHYDRATES, ETC., AND OTHER SUBSTANCES INSOLUBLE OR VERY SLIGHTLY SOLUBLE IN WATER.

Concentrated neutral or slightly alkaline liquor in relatively small quantity is used as an emulsifying agent instead of soaps, resins, alkalies, etc. When the water is evaporated a substance is obtained which is insoluble or soluble with difficulty. The emulsion may be mixed with neutral and acid salt solution. For 250 grammes (0.55 lb.) concentrated liquor 1250 grammes (2.76 lb.) of a solution of asphalt in tar or tar oil may be used.

German Patent 250275 (1911).
Chem. Zentr. (1912) part II p. 779.

Platsch, M.—BINDER FOR BRIQUETTES MADE FROM WASTE SULPHITE LIQUOR BY REMOVAL OF LIME WITH SULPHURIC ACID IN SLIGHT EXCESS.

Addition of sulphuric acid to the liquor, during which an increase in temperature is to be prevented.

German Patent. Appl. 28865 (1911).

Mathesius, W.—IMPROVING THE BRIQUETTING AND AGGLOMERATION OF IRON ORE.

The possibility of reduction is more favourable with briquettes. Great saving in coke (15 per cent) and increase of production.

Chem.-Ztg. vol. 37 (1913) p. 625.

Platsch, M.—PURIFICATION OF CONCENTRATED WASTE SULPHITE LIQUOR.

The liquor concentrated to a syrupy consistency is mixed in the cold with sulphuric acid corresponding to the lime content, and the free acid afterwards saturated with bases or basic salts after removal of the gypsum.

English Patent 19600 (1912).
German Patent 286210 (1911).
United States Patent 1054041 (1913).
Chem. Abs. vol. 7 (1913) p. 1414, vol. 8 (1914) p. 572 vol. 10 (1916) p. 1269.

BINDING MATERIAL FROM WASTE SULPHITE LIQUOR.

Concentrated liquor is treated with creosote oil.

United States Patent 877414.

Cushman, A. S.—CHEMICAL CONTRIBUTION TO THE ART OF ROAD CONSTRUCTION.

Waste sulphite liquor is emulsified with mineral oil in order to render it more water-resistant when used as a road-binder.

J. Soc. Chem. Ind. vol. 30 (1911) p. 211.

THE DISPOSITION OF WASTE SULPHITE LIQUORS.

A discussion appearing in Papier Zeitung and Frankfurter Zeitung, refers principally to the use as a binding agent.

Paper vol. 9 (1912) No. 10 p. 22, vol. 10 (1912) No. 1 p. 19.

Ellis, C.—CONCENTRATION OF WASTE SULPHITE LIQUOR FOR PREPARATION OF A ROAD-BINDER.

The liquor is neutralized with lime and aerated for the purpose of removing the methyl alcohol. The liquor is then fermented and the spirit distilled off, and the remaining liquor concentrated to 30°Bé.

United States Patent 1042538 Oct. (1912).
J. Soc. Chem. Ind. vol. 31 (1912) p. 1120.

Pollacsek, E.—PROCESS FOR MANUFACTURING A WEATHER-RESISTANT COAL FUEL, SIMULTANEOUSLY RENDERING THE SULPHUR PRESENT IN THE COAL HARMLESS.

Coal is mixed with milk of lime containing starch, glue or waste sulphite liquor, the mixture dried, and the briquettes herefrom immersed in a mixture obtained by heating crude petroleum oil, containing paraffin or ozekerite substances, with bitumen and phenols at boiling temperature under strong aeration, until a mixture is obtained which solidifies on cooling.

German Patent 264783 (1912).

Pollacsek, E.—PROCESS FOR MANUFACTURING A WEATHER-RESISTANT COAL FUEL, SIMULTANEOUSLY RENDERING THE SULPHUR PRESENT IN THE COAL HARMLESS.

The coal is mixed with a mixture consisting of a little more lime than necessary to bind the sulphur and of a binding material (starch, glue, sulphite waste liquor, etc.) This mass is mixed with the hot impregnating liquid, whereby a plastic mass is obtained which after drying is waterproof throughout.

German Patent 266401 (1913) addition to German Patent 264783.

Grempe, P. M.—UTILIZATION OF WASTE SULPHITE LIQUORS.

The unconcentrated liquor used for road-binding can be transported in Germany according to a special tariff.

Wochbl. Papierfabr. vol. 43 (1912) p. 3417.

Buisson, J.—UTILIZATION OF WASTE WOOD.

The wood is ground and made into briquettes with waste sulphite liquor. The mixture is carbonized at 350° and cooled in the absence of air.

French Patent 449350 (1912).

Graetz, B.—BRIQUETTING OF COAL WITH WASTE SULPHITE LIQUOR BY ADDITION OF INORGANIC SUBSTANCE.

Coal dust is mixed with sulphite liquor with an addition of aluminium hydrate, preferably in the gelatinous condition.

German Patent 211479 (1912).
Chem.-Ztg. vol. 38 (1914) Rep. p. 175.
J. Soc. Chem. Ind. vol. 33 (1914) p. 471.

Kausch.—ADHESIVE AND BINDING MATERIALS.

A review of patented methods for utilization of waste sulphite liquor.

Kunststoffe vol. 3 (1913) pp. 112, 127.

Sorge, K., and Weiskopf, A.—IMPROVING BRIQUETTING AND AGGLOMERATION OF IRON ORES AND DUST FROM BLAST FURNACES.

In a discussion of the utilization of lower grade ores and various briquetting processes the cell-pitch briquettes are also mentioned.

Chem.-Ztg. vol 37 (1913) p. 7.

Aufhauser, D.—CELL-PITCH.

Manufacture and composition

Water	11·32	per cent
Ash	15·03	"
C	36·21	"
H	4·44	"
S (combustible)	3·32	"
N	0·43	"
O	29·25	"
	100·00	"

Heat value 3,166 calories (5,700 B. T. U. per lb.) (HP = 4,391 calories). The price of 40 marks per metric ton ($8.64 per short ton) comes too close to the price of tar.

However, the addition of cell-pitch to fine coal is lower (5 per cent) than that of tar pitch (7-10 per cent). Cell-pitch is at the present time of importance in the manufacture of ore briquettes. In the blast furnace about 15 per cent of cell-pitch briquettes from furnace dust are added.

Z. angew. Chem. vol. 25 (1912) p. 74.

Voitel, K.—WASTE SULPHITE LIQUOR AS A DUST-BINDER.

The liquor was sprinkled on the roads in the vicinity of the pulp-mill in Grodlitz (Saxony) and showed the qualities of a good dust-binder such as $CaCl_2$. Its action was still noticeable after 6 or 8 weeks. Leather, iron or rubber are not attacked.

Rauch Staub. vol. 2 (1912) p. 252.
Wasser Abwasser vol. 6 (1913) p. 144.
Chem. Abs. vol. 7 (1913) p. 692.

Platsch, M. and Hoesch and Co.—

The concentrated waste lyes are treated in the cold with a slight excess of sulphuric acid and the precipitated calcium sulphate is recovered. It is sometimes necessary to cool the lyes specially, in order to avoid coagulation of the agglutinating substances liberated by the acid before the briquettes are made. The briquettes made with the purified lyes are dried at a temperature of about 100° C. and a reaction takes place whereby the agglutinating substances are fixed in an insoluble form, whilst the slight excess of sulphuric acid is decomposed and escapes as sulphur dioxide together with the volatile organic acids of the lyes. These acids, being driven off in a concentrated form, may be recovered.

French Patent 455059 (1913).
Norwegian Patent 26296 (1915).
J. Soc. Chem. Ind. vol. 32 (1913) p. 864.
Papier-Ztg. vol. 39 (1914) p. 1988.
Papir J. vol. 3 (1915) p. 262.

Robeson, J. S.—UTILIZING SULPHITE LYE FOR ROAD-MAKING.

(1) Roads comprising clays or clayey matter are treated first with finely divided calcareous material and then with an acidified sulphite waste liquor preparation, preferably containing some sodium lignosulphonate. (2) Salt is substituted for calcareous matter and the sulphite waste liquor is used in a concentrated form.

United States Patents 1075856 and 1075857 (1913).
J. Soc. Chem. Ind. vol. 32 (1913) p. 1070.

Walker, W. O.—THE PROBLEM OF THE WASTE LIQUOR FROM SULPHITE PULP-MILLS.

Most of the uses that have been proposed have been abandoned, either on account of the cost or of unsuitability for the purposes intended. During the winter of 1910-11 an investigation into the possible use of the liquor for laying of dust of roads was carried on at Queens University, Kingston, Ontario, by R. T. Mohan. Small sample roads were constructed in imitation of the common macadam road. A layer of road dust was placed on top. Three such roads were treated, one with ordinary road oil, another with the same quantity of concentrated (4:1) waste liquor, and the third with road oil followed by waste liquor. These roads were treated with water at intervals of a few days for a period of four months, using a total of ten inches of water, the most at any one time being 2½ inches. These figures correspond closely to the total and maximum rainfall in Ontario during May, June, July, August, and September. The result was that the oil on the first road was practically all washed away, while the second road that was treated with the liquor and the third road treated with liquor and oil still presented a hard surface, which after being broken and dried showed very little dust and did not have the disagreeable odour given off from the oil-treated road.

This experiment gives promise of the material finding use in the treatment of roads. The cost, especially in the neighbourhood of pulp-mills, should not be prohibitive.

J. Soc. Chem. Ind. vol. 32 (1913) p. 389.
Paper vol. 11 (1913) No. 9 p. 21.
(See " General " p. 185.)

Robeson, J. S.—PROCESS FOR TREATING ROADS.

With the object of compacting the surfaces of roads containing clay or clay-forming material, and preventing the formation of dust upon the same, the roads are sprinkled with sulphite waste liquor, the latter being used either in the very concentrated form, somewhat diluted and neutralized, or combined with alumina. (See also United States Patent 1,069,031.)

United States Patents 1069029 and 1069030 (1913).
J. Soc. Chem. Ind. vol. 32 (1913) p. 869.

Robeson, J. S.—PLASTIC SUBSTANCES FROM WASTE LYES.

As a binding material for finely divided inert substances claim is made for a mixture of sulphite liquor and neutral plastic clayey matter pulped together.

United States Patent 1069031 (1913).
J. Soc. Chem. Ind. vol. 32 (1913) p. 864.

Ellis, C.—ROAD-BED CONSTRUCTION.

The road material is incorporated with a binder consisting of dry sulphite liquor solids and a weighty material. The binder may also be dusted over the road surface.

United States Patent 1068084 (1913).
J. Soc. Chem. Ind. vol. 32 (1913) p. 829.

Pollacsek, E.—UTILIZATION OF SULPHITE LYES AS BINDING SUBSTANCE.

The spent lyes are treated with a slight excess of lime and evaporated until a scum begins to form; a certain quantity of heavy mineral oil is then added drop by drop, which enables the compounds of lime to be skimmed off. The clarified liquid is further evaporated until it is just fluid, and about 5 per cent of heavy mineral oil is worked into the hot thickened mass. After cooling, the mass is mixed with a further quantity of heavy oil in the proportion of 5 parts of oil to 4 parts of the product; the whole is mixed with 1.5 part of lime paste and boiled again. This product serves as a basis for binding and impregnating compounds by mixing with lime, heavy oil or water according to the purpose in view.

French Patent 462429 (1913).
United States Patent 1133499 (1915).
Norwegian Patent 24349 (1914).
J. Soc. Chem. Ind. vol. 33 (1914) pp. 248, 746, vol. 34 (1915) p. 488.
Chem. Abs. vol. 9 (1915) p. 1391.
Papir J. vol. 2 (1914) p. 138.
Tidskrift vol. 4 (1914) p. 191.

Muller, P. G.—BINDING MATERIAL FROM SULPHITE LYES.

Waste lyes from the manufacture of sulphite cellulose are concentrated and then incorporated by prolonged stirring with carbon bisulphide; the material is suitable for use as a varnish, paint, covering or binding medium for briquettes. In the manufacture of coal briquettes with this material, oil, resin, wax, paraffin, camphor, etc., may be added, with the carbon bisulphide in the dissolved state, as a protection against moisture and disintegration in the fire.

English Patent 7324 (1913).
J. Soc. Chem. Ind. vol. 33 (1914) p. 478.
Paper vol. 14 (1914) No. 13 p. 23.

Pollacsek, E.—SULPHITE LIQUOR BRIQUETTES.

Papier-Ztg. vol. 39 (1914) p. 1616.

Ellis, C.—COMPOSITION FOR LAYING ROAD-DUST.

An emulsion of concentrated waste sulphite liquor of 30°Bé. (sp. gr. 1.263), a hygroscopic softening agent, and a non-tarry petroleum oil, the last named not exceeding 25 per cent.

United States Dept 1,119,500 (1914).
J. Soc. Chem. Ind. vol. 34 (1915) p. 82.

Graetz, B.—COAL BRIQUETTES WITH WASTE SULPHITE LIQUOR AS BINDING MATERIAL.

Fine coal is mixed with powdered blast-furnace slag, plaster of Paris, cement or like material capable of combining with water and holding it in combination at a temperature up to 110°C; the mass is mixed with about 14 per cent of sulphite-cellulose waste lye containing 50 per cent H_2O heated and formed into briquettes which are heated to carbonize the sulphite lye.

German Patent 280,455 (1913).
J. Soc. Chem. Ind. vol. 34 (1915) p. 540.

Bibb, D. H.—PROCESS OF MAKING COHERING MASSES FROM WASTE SULPHITE LIQUOR.

The waste liquor is evaporated to give a residue of a soluble pitch, which is powdered and mixed with granular material and a solvent, e.g. water. The mixture is formed into briquettes and converted by the application of heat into a non-coked material resistant to water.

United States Patent 1158364, 1158365, 1158366 (1915).
Norwegian Patent 27881 (1917).
J. Soc. Chem. Ind. vol. 34 (1915) p. 1119.
Papier-Fabr. vol. 5 (1917) No. 13 p. 111.

Walsh, J. P.—PROCESS OF BINDING ROADS AND ROAD-BEDS AND COMPOSITION THEREFOR.

A highly hygroscopic road-binder is made from a comminuted solid obtained from waste sulphite liquor and an insoluble carbonaceous filler, e.g. the waste product from the manufacture of soda ash. The binder and filler are applied to the road-bed and the whole is then treated with water.

United States Patent 1178979 (1916).
J. Soc. Chem. Ind. vol. 35 (1916) p. 636.

Jabs, A.—PROCESS OF MAKING DRY BRIQUETTES CONTAINING SULPHITE LIQUOR RESISTANT TO WEATHER.

The material is subjected to the action of waste gases from gas engines, furnaces, etc., or other gases containing carbon dioxide at a temperature below 120° C., until sufficiently weather-proof and dry, a suitable temperature being obtained by mixing the used gas with fresh, hot, combustion gases.

German Patent 287015 (1912).
J. Soc. Chem. Ind. vol. 35 (1916) p. 103.

Winthol, A. G.—PROCESS OF MAKING PEAT BRIQUETTES WHICH WILL RETAIN THEIR FORM UNTIL BURNT.

Finely divided peat moss is added to the peat and binding material, e.g. concentrated sulphite liquor. The product retains its form during combustion and is, hence, completely burnt with a maximum development of heat.

German Patent 287016 (1913).
J. Soc. Chem. Ind. vol. 35 (1916) p. 103.

Freeman, W. K.—INSULATING MATERIAL, PLASTIC COMPOSITION, AND CEMENT COMPOSITION FROM WASTE SULPHITE LIQUOR.

United States Patent 1175422-1175426 (1916).
(See " Miscellaneous " p. 168.)

United States Consul, Berlin.—CELL-PITCH MANUFACTURE IN GERMANY.

General description of process of manufacture with analysis of thickened residues and dry substances.

Paper Trade J. vol. 63 No. 22 (1916) p. 48.

Woodrop, L. H. (Robeson Process Co.).—BINDER FOR BRIQUETTES.

The composition consists of an intimate mixture of bituminous coal, dried waste sulphite liquor, bituminous matter such as pitch, and an inert granular material such as sand.

United States Patent 1221259 (1917).
J. Soc. Chem. Ind. vol. 36 (1917) p. 540.

GUMS, ADHESIVES, AND SIZING MATERIALS

In the preceding chapter it was shown that the evaporated sulphite liquor can be used either alone or in mixture with other substances as a binding material. It has also been suggested to use the waste sulphite liquor remaining after fermentation and production of alcohol for paper-sizing, in mixture with rosin soap.

Cross and Bevan showed as early as 1883 that when gelatin or albumen is added to the waste sulphite liquor substances are precipitated which they called respectively "gela-lignosin" and "albu-lignosin," both of which are suitable for use as size, mordants, etc.

The product is similar to that obtained by Ekman's patents, according to which a "dextrone" is produced by evaporating the liquor after it is made alkaline and adding to the acidified, concentrated liquor soluble salts such as the chloride or sulphate of sodium. If this product is mixed with gelatin or glue a compound is obtained which can be dissolved and used as a mordant or size.

Mitscherlich's "Gerbleim" or "tannin size" is, like the "lignosin" formed by precipitation of the acid sulphite liquor with glue or albuminous bodies. The substance can be dissolved in alkaline solution and reprecipitated by the addition of alum. The product is recommended as a paper size in mixture with rosin size. The numerous patents connected with this process show in detail how the size is prepared.

According to Mitscherlich's German Patent 235965 a suitable emulsion for paper-sizing is prepared as follows: A solution of horn in soda is mixed with sulphite liquor, previously treated with sodium sulphate, and the mixture precipitated with hydrochloric acid. The precipitate is washed out and dissolved in borax. Rosin size is added to this solution, whereupon an emulsion is obtained which, diluted with water, can be precipitated with alum or with rock-salt.

Adhesives may also be produced by concentrating the waste liquor to which carbonate or oxide of zinc has been added, or by concentrating in vacuo with an excess of magnesium oxide and adding magnesium chloride in a proportion equivalent to the amount of magnesium oxide remaining in excess, to form the oxychloride.

It is claimed that resinous matters can be obtained from waste sulphite liquor by hydrolysis in a container divided by a diaphragm. A treatment of the liquor with chlorates in order to remove the tannic acid, and a subsequent concentration of the liquors with protein substances in order to produce an adhesive substance, is recommended by Katz and by Schweinburg.

Tilghman, B. C.—UTILIZATION OF WASTE SULPHITE LIQUOR FOR FERTILIZING PURPOSES.

English Patent 2924 (1866).
United States Patents 70485 (1867) and 92220 (1869).
(See "Fertilizer" p. 141.)

Mitscherlich, A.—ADHESIVE SUBSTANCES.

The author calls attention to the presence of substances in the waste sulphite liquor which could be used as a gum.

Kirchner, Holzzellstoffabrikation 1907 p. 19.

Mitscherlich, A.—PROCESS FOR THE PREPARATION OF TANNIN FROM OAK.

German Patent 4179 (1878).
English Patent 1668 (1882).
(See "Tanning Materials" p. 78.)

Mitscherlich, A.—INNOVATIONS IN THE PROCESS OF PRODUCING TANNING MATERIALS WITH THE PRODUCTION OF THE BY-PRODUCTS, CELLULOSE, GUMS, ACETIC ACID, AND CALCIUM BISULPHITE.

German Patent 4179 (1878).
Addition to German Patent 4178 (1878).
(See "Tanning Materials" p. 78.)

Mitscherlich, A.—COOKING OF WOOD WITH CALCIUM BISULPHITE, RECOVERING CELLULOSE, TANNING MATERIALS, GUMS, AND ACETIC ACID.

English Patent 1668 (1882).
(See "Tanning Materials" p. 78.)

Cross and Bevan.—IMPROVEMENT IN THE MANUFACTURE OF MORDANTING AND FINISHING MATERIALS FOR TEXTILE FABRICS, PAPER, ETC. (GELA-LIGNOSIN).

English Patent 1548 (1883).
(See "Dye" p. 148.)

Pictet and Brelaz.—IMPROVEMENTS IN SULPHITE WOOD-PULP.

Recovery of gum, rosin, tannin, alcohol, etc.

English Patent 9509 (1884).
(See "Tanning Materials" p. 78.)

Leonhardt, H. (A. Mitscherlich).—PROCESS FOR SIZING PAPER.

Process for sizing paper materials in which the rosin soap or animal size in the pulp is precipitated by tannin substances.

German Patent 34420 (1885).

Mitscherlich, A.—IMPROVEMENTS IN SIZING PAPER.

Relates to the sizing of paper with materials such as the extract obtained when spruce (*Picea excelsa*) is subjected to a process of sulphite boiling. "By this new method of sizing certain paper materials special advantages are obtained. For instance in sizing the sulphite cellulose by the use of a sufficient quantity of this glue material (extract and resin soap) under otherwise identical conditions, I get, by the hereinafter described proceeding, a transparent and very strong product, which comparatively, is not too brittle, and similar to the paper parchment." If paper sized by this process be further filled with a body like linseed oil, the inventor claims an increase in strength up to 70 per cent, and nearly perfect transparency. The use of such paper is suggested for tracing purposes, for use instead of translucent panes of glass, and generally for the uses to which such transparent papers as are intended to give protection against atmospheric influences at a very low expense are put, also for the manufacture of board and papier-mâché textures.

English Patent 12566 (1884).
J. Soc. Chem. Ind. vol 4 (1885) p. 550.

Nettl, A. S.—PROCESS FOR TRANSFORMING THE WASTE LIQUORS FROM THE MANUFACTURE OF SULPHITE CELLULOSE INTO SUBSTANCES AVAILABLE TO THE INDUSTRY.

The liquor is neutralized with milk of lime or calcium carbonate or other base, concentrated and cooled down, forming a gummy paste which can be used as an adhesive, binding or concentrating material, etc., replacing glue starch, dextrine, etc.

Austrian Privilegium 1576 (1888).

Mitscherlich, A.—NEW PROCESS FOR SIZING PAPER.

On adding sulphite liquors, in which wood has been boiled, to a solution of gelatin, the latter is precipitated in a "highly cementitious and adhesive condition." The precipitate is dissolved in slightly alkaline water and is reprecipitated in the pulp by the addition of alum. (Compare J. Soc. Chem. Ind. vol. 2 (1883) p. 541.)

English Patent 11372 (1890).
J. Soc. Chem. Ind. vol. 10 (1891) p. 787.

Mitscherlich, A.—PROCESS FOR SIZING PAPER.

Glue or albuminous bodies are added to sulphite liquor. The precipitate is dissolved in acid-free or alkaline water and is added to paper. The paper contains a small quantity of acid or salts in order to change the substance into a strongly sizing form.

German Patent 54206 (1890).
Addition to German Patent 34420 (1885).
Ber. (1891) p. 343.

Mitscherlich, A.—PROCESS FOR PRODUCTION OF TANNING MATERIALS, ADHESIVES, AND OTHER SUBSTANCES FROM WASTE SULPHITE LIQUOR BY OSMOSIS.

German Patent 72161 (1891).
English Patent 12927 (1893).
(See "Tanning Materials" p. 78.)

Mitscherlich, A.—PROCESS FOR PREPARATION OF ADHESIVES, BINDING, AND CONCENTRATING MATERIALS FROM WASTE SULPHITE LIQUORS.

German Patent 72362 (1891).
(See "Binding Material" p. 52.)

Jürgensen, F., Niesz. Fr., Gümbel, G.—ADHESIVE LIKE THAT PRODUCED BY PATENT 72386, ESPECIALLY FOR COATING CONTAINERS FOR PETROLEUM, ETC.

Concentrated waste sulphite liquor is mixed with glue or other materials with the addition of hydraulic lime or cement. When the container for petroleum is coated with the substance a paste which remains soft and plastic is obtained under the influence of the liquor.

German Patent 73718 (1892).
Ber. vol. 27 (1894) p. 445.

Saxl, J. and Oberländer, L.—PROCESS FOR PREPARATION OF A WATER-RESISTANT ADHESIVE.

The waste liquor is treated with a solution of a protein substance (chondrin, glutin, glue, blood, albumin, casein, fibrin) and a dilute acid (sulphuric) or the solution of a salt of acid reaction (alum, ferrous sulphate).

German Patent 63042 (1891).
Z. angew. Chem. vol. 5 (1892) p. 382.

Ekman, C. D.—IMPROVEMENTS IN OBTAINING USEFUL PRODUCTS FROM THE LIQUORS RESULTING FROM THE MANUFACTURE OF CELLULOSE BY THE SULPHITE PROCESS.

English Patent 20036 (1893).
Austrian Privilegium 569 (1894).
(See "Dye" p. 148.)

Mitscherlich, A.—PROCESS FOR PREPARATION OF ADHESIVES FROM HORN SUBSTANCES BY MEANS OF WASTE SULPHITE LIQUOR.

Waste liquor, or the tanning material obtained therefrom, precipitates in acid solution a keratin tanning substance from a solution of keratin substances. The precipitate is dissolved in dilute soda solution.

One method is to have the keratin substances in finely-divided form in the acid waste liquor until they are easily soluble in dilute soda solution. Keratin substances like horns, claws, and hoofs are dissolved in water above 100°C. The undissolved substances are dissolved in dilute sodium hydroxide. The solutions are precipitated by the tannin contained in the liquor. When the tannins are removed the liquor can be used for the production of alcohol.

German Patent 82498 (1893).
Ber. vol. 28 (1895) p. 869.
Papier-Ztg. vol. 20 (1895) part II p. 2716.
Hofmann, C., Handbuch der Papierfabrikation 2nd Edition (1897) p. 1619.

Mitscherlich, A.—PROCESS AND APPARATUS FOR UTILIZATION OF WASTE SULPHITE LIQUOR.

Includes Mitscherlich's German patents for producing adhesives, tanning materials, fermentable sugars, and fodder from waste sulphite liquor.

Austrian Privilegium 112 (1894).

Kuhn, R.—ON FAVOURABLE EXPERIENCE WITH MITSCHERLICH'S "GERBLEIM" IN CONTRAST WITH RESIN SOAP.

Papier-Ztg. vol. 20 (1895) pp. 1083, 1351, 1445.

Mitscherlich, A.—PROCESS FOR PREPARATION OF ADHESIVES FROM HORN SUBSTANCES WITH WASTE SULPHITE LIQUORS.

A clear solution of horn is obtained by treating it with slowly circulating water which is heated above 120°C. The precipitation of the horn solution is effected with neutralized waste sulphite liquor in very dilute form, in order to obtain pure compounds.

German Patent 86651 (1895).
Addition to German Patent 82498 (1893).
Ber. vol. 29 (1897) p. 452.
Papier-Ztg. vol. 21 (1896) part II p. 1848.

Mitscherlich, A.—TANNIN GLUE AND PAPER-SIZE PREPARATION, QUALITIES, AND USES.

Papier-Ztg. vol. 20 (1895) pp. 466, 529.

Ekman, C. D.—WASTE SULPHITE LIQUOR.

A review of various methods for utilization. No practical results obtained with the paper size prepared from waste liquor by Mitscherlich's method.

The "gela-lignosin" from sulphite liquor (Cross and Bevan 1883) has been so far perfected that it may be used for the sizing of high grade white papers. Better results are obtained than with rosin-size with regard to strength. The only drawback is the high price when manufactured on a large scale.

Papier-Ztg. vol. 21 (1896) part I pp. 2218, 2609, 3247.
J. Soc. Chem. Ind. vol. 15 (1896) p. 735.

Mitscherlich, A.—REPLY TO EKMAN'S STATEMENTS.

Papier-Ztg. vol. 21 (1896) pp. 2349, 2850.

Farbwerke Friedrichsfeld, Remy, P.—WATERPROOFING PAPER BY WASTE SULPHITE LIQUOR.

To the evaporated liquor are added solutions of ferrous, ferric or lead salts in quantities equivalent to the calcium content. Paper treated with this solution is made waterproof on heating at 70° to 130°C.

Lead salts are poisonous and should not be used. The discolouring of the paper due to the brown colour of the liquor can be removed by washing.

German Patent 90798 (1896).
Papier-Ztg. vol. 22 (1897) part I p. 426.
J. Soc. Chem. Ind. vol. 16 (1897) p. 630.

Mitscherlich, A.—PROCESS FOR PREPARATION OF ADHESIVE SUBSTANCES FROM HORN SUBSTANCES WITH WASTE SULPHITE LIQUOR.

Keratin or substances containing similar matters are dissolved in waste liquor which has previously been treated with soda or potash and lime, or with sodium or potassium hydroxide.

German Patent 93944 (1896).
Extension of German Patent 82498.
Papier-Ztg. vol. 22 (1897) p. 3074.
Chem. Zentr. (1897) part II p. 1126.

Mitscherlich, A.—PROCESS FOR PREPARATION OF ADHESIVES FOR PAPER SIZING.

Rosin is dissolved in a solution of horn in waste sulphite liquor. Horn and rosin are separately dissolved in waste liquor containing hydroxide or carbonate of alkalies, and the solution of horn or rosin in alkali hydroxide or carbonate mixed with waste liquor.

German Patent 93945 (1896).
Papier-Ztg. vol. 22 (1897) part II p. 3148
Chem. Zentr. (1897) part II p. 1126.

Bloesch, K.—A MIXTURE FOR COATING CONTAINERS FOR PETROLEUM, ETC.

Consists of 70 parts waste liquor, 5 parts carpenters' glue, and 25 parts lime.

Russian Privilegium 558 (1898).
Chem.-Ztg. vol. 23 (1898) p. 320.

Ekman, C. D.—PROCESS FOR PRODUCTION OF ADHESIVE AND SIZING SUBSTANCES FROM WASTE LIQUOR.

Carbonate or oxide of zinc is added directly to the waste liquor, or the zinc oxide is formed in the liquor by precipitation of a soluble zinc salt with a suitable base such as sodium carbonate, and the liquor is evaporated.

German Patent 109951 (1899).
Austrian Patent 3229 (1899).
English Patent 189 (1899).
Papier-Ztg. vol. 25 (1900) p. 797.
J. Soc. Chem. Ind. vol. 18 (1899) p. 1150.

Brookes, A. G. (From Trippe, W.)—TREATMENT AND UTILIZATION OF WASTE SULPHITE LIQUOR.

The liquor is concentrated by evaporation until the sulphur compounds become decomposed and escape in a gaseous state, whilst the residue remains in form of a dry substance. In order to avoid frothing or formation of a skin on the surface of the liquor, preventing the gas escaping, it is proposed that substances such as carbohydrates, albuminoids, albuminates, terpenes, resins, tar products, organic acids or esters shall be added at the critical stage. This also reduces the hygroscopicity of the residue without diminishing its adhesiveness. The employment of solutions of resin in benzine or petroleum is specially claimed. If desirable the mineral constituents are separated from the liquor. It is claimed that this residue may be employed as a substitute for pitch or resin and as a manure.

English Patent 8088 (1901).
J. Soc. Chem. Ind. vol. 20 (1901) p. 741.

Katz, A.—PROCESS FOR PREPARATION OF ADHESIVE SUBSTANCES.

The liquor freed from SO_2 and sulphites is heated under pressure with alkali chlorates until a test shows that the tannic acid in the liquor has been changed into gallic acid and sugar. The neutralized filtrate is mixed with from 10-30 per cent glue and is evaporated.

German Patent 149461 (1903).
Papier-Ztg. vol. 29 (1904) part I p. 800.
Jahrb. Chem. Techn. (1904) part II p. 523.

Schweinburg, A.—PROCESS FOR PREPARATION OF A WATER-SOLUBLE ADHESIVE SUBSTANCE FROM WASTE SULPHITE LIQUORS.

Liquor freed from SO_2 and sulphite is boiled with the required amount of chlorate and a mineral acid till the tannic acid is entirely destroyed. Then the liquor is heated with protein substances and dried.

Austrian Patent 14423 (1902).

Rogers, J. J.—SIZING MATERIAL.

Waste sulphite liquors are concentrated in absence of air according to Robeson's process (Austrian Patent 42479) for preparing of sizing material.

Paper Trade Review vol. 31 No. 12 (1904).

Kruger, F.—ADHESIVES, GUMS.

Discussion of Mitscherlich's, Ekman's, and Nettl's products.

Verhandl. d. Vereins z. Beford, d. Gewerbfleisses.
Mon. sci. (4) vol. 19 part II (1905) p. 801.
Farben-Ztg. vol. 11 (1906) p. 237.

CELLULOSE ADHESIVE SUBSTANCES.

Mentions the various adhesives that have been proposed to be made from sulphite liquor.

Z. ges. Textilind vol. 8 (1905) p. 691.
Z. angew. Chem. vol. 19 (1906) p. 302.

Mitscherlich, A.—PREPARATION OF A PAPER-SIZING MATERIAL.

Sulphite liquor to which has been added sodium sulphate to overcome the harmful effects of the lime is mixed with a solution of resin and horn which has been prepared under 100° by dissolving horn in rosin size containing excess of soda.

German Patent 169408 (1903).
Papier-Ztg. vol. 31 (1906) part I p. 1732.
Jahrb. Chem. Techn. (1906) part II p. 546.
Wochbl. Papierfabr. vol. 37 (1906) p. 1857.

Mitscherlich, A.—PREPARATION OF PAPER SIZE.

Zinc is added in the form of a fine powder to the rosin size solution and the sulphite liquor, which has the effect of producing a light colour.

German Patent 169409 (1904) addition to German Patent 169408.
Papier-Ztg. vol. 31 (1906) part I p. 1732.
Jahrb. Chem. Techn. (1906) p. 546.
Wochbl. Papierfabr. vol 37 (1906) p. 1858.

Elb, M.—PREPARATION OF A GLUE-LIKE SUBSTANCE.

To avoid the separation of salts during the evaporation of sulphite liquor, formaldehyde is added to the liquor (about 3.5 per cent). The action of the aldehyde is not clear. Probably the aldehyde combines with the sulphite to form substances which are crystallized with difficulty. The product of the evaporation may be decolorized with alkalies.

German Patent 166947 (1905).
Austrian Patent 23046 (1905).
Papier-Ztg. vol. 31 (1906) part I p. 125.
Chem. Zentr. (1906) part I p. 801.

Robeson, J. S.—PROCESS FOR TREATMENT OF WASTE SULPHITE LIQUOR.

Neutralization and subsequent evaporation in absence of air. When no excess of alkali, a comparatively clear and permanent viscoid liquid is obtained with a high adhesive and binding power.

British Patent 17956 (1908).
Austrian Patent 42479 (1906).
Papier-Ztg. vol. 30 (1905) part I p. 266.
Chem. Abs. vol. 4 (1910) p. 669.

Robeson, J. S.—ADHESIVE COMPOUND FROM SULPHITE LIQUOR.

Waste sulphite liquor from the digestion of spruce wood is neutralized by milk of lime and concentrated in vacuo to a density of about 30°Bé. to form an adhesive product soluble in water, clear or translucent, and in concentrated solution, not precipitating glue solution.

United States Patent 833634 (1906).
English Patent 22887 (1906).
J. Soc. Chem. Ind. vol. 25 (1906) p. 1115, vol. 26 (1907) p. 340
Chem. Abs. vol. 1 (1907) p. 498

Massot, W.—REVIEW OF NEW ADHESIVE SUBSTANCES.

Mentions Katz's, Ekman's, Cross and Bevan's, and Mitscherlich's processes for producing adhesive substances. No comment is made.

Z. angew. Chem. vol. 19 (1906) p. 177.

Kumpfmiller, A.—PROCESS FOR PURIFICATION OF WASTE SULPHITE LIQUOR.

Austrian Patent 40657 (1906).
(See "Miscellaneous" p. 168.)

ROSIN SIZE OR TANNIN SIZE ("GERBLEIM").

"Gerbleim" colours the paper too much, it is too expensive, contains harmful compounds, and dulls the paper.

Papier-Fabr. vol. 4 (1906) pp. 400, 791.
Z. angew, Chem. vol. 19 (1906) p. 1270.

WASTE SULPHITE LIQUOR AS A FILLER FOR ROSIN SOAPS.

Wochbl. Papierfabr. vol. 37 (1906) p. 814.

Robeson, J. S.—ADHESIVE MATERIALS FROM WASTE SULPHITE LYES.

Farinaceous vegetable materials, such as boiled wheat flour rich in protein, are intimately mixed with unaltered waste sulphite liquors and evaporated to a suitable consistency.

United States Patent 851378 (1907).
J. Soc. Chem. Ind. vol. 26 (1907) p. 634.
Chem. Abs. vol. 1 (1907) p. 1640.

Robeson, J. S.—

In the composition described in the preceding abstract, a soluble albuminoid or animal glue may be substituted for farinaceous materials.

United States Patent 851379 (1907).
J. Soc. Chem. Ind. vol. 26 (1907) p. 634.

Robeson, J. S.—

Boiled starchy materials, molasses or dextrin, are incorporated either singly or together with concentrated sulphite liquor.

United States Patent 851380 (1907).
J. Soc. Chem. Ind. vol. 26 (1907) p. 634.

Robeson, J. S.—

A concentrated sulphite solution of non-woody tissue (waste sulphite lyes) is mixed with the condensed liquid obtained from the destructive distillation of wood, and heated till homogeneous.

United States Patent 851381 (1907).
J. Soc. Chem. Ind. vol. 26 (1907) p. 634.

Mitscherlich, A.—EMULSIONS SUITABLE FOR SIZING PAPER.

By the process described in French Patent 356269 of 1905 (J. Soc. Chem. Ind. (1905) p. 1320) it was not possible to obtain a homogeneous liquid unless only relatively small quantities of sulphite-cellulose waste lye were added to the mixed animal and rosin size, in presence of sodium carbonate at 30°—60° C., a stable emulsion is formed which can be used for sizing paper in the usual manner. Viscous substances may also be added to improve the stability of the emulsion.

German Patent 220066 (1908).
J. Soc. Chem. Ind. (1910) p. 483.

Kitsee, I.—TREATING SPENT LIQUOR.

The liquor is placed in the positive (anode) compartment of an electrolytic apparatus and a solution of salt is introduced into the negative (cathode) compartment. A current of electricity is passed through the solutions causing the solution in the cathode compartment to become alkaline in reaction, whilst the "intercellulose" and resinous matters are retained in the anode compartment. It is claimed that in this way the caustic and resinous matters of the spent liquor are recovered.

United States Patent 942207 (1909).
J. Soc. Chem. Ind. vol. 29 (1910) p. 83.
Chem. Abs. vol. 4 part 1 (1910) p. 668.

Klason, P.—MINERAL SIZING USING SULPHITE LIQUOR.

Using aluminium silicate the paper loses its gloss. This is avoided by using sulphite liquor for precipitation instead of aluminium sulphate, and hence calcium silicate is produced.

Papier-Ztg. vol. 34 (1909) part I p. 1315.
Papier-Fabr. vol. 7 (1909) p. 445.
Z. angew. Chem. vol. 22 (1909) p. 1423.

Hough, Wm. J.—RECOVERING RESINOUS MATTER FROM WASTE SULPHITE LIQUOR.

A solidification of the resin in the condition of a resinate adapted to be readily dissociated from the residual liquor.

English Patent 19116 (1909).
Chem. Abs. vol. 5 (1911) p. 1839.

Robeson, J. S.—ADHESIVE.

The waste liquors are neutralized with alkalies or lime and evaporated by use of inert gases.

Austrian Patent 42479.

Robeson, J. S.—UTILIZATION OF WASTE SULPHITE LIQUOR.

Since 1904 a powder known as "Glutrin" has been manufactured in the United States and is obtained by concentrating waste sulphite liquor to dryness.

Paper vol. 8 (1911) No. 9 p. 63.

KLASON'S MINERAL SIZING WITH WASTE SULPHITE LIQUOR.

There is no information regarding this sizing as it has not met with much interest among the paper manufacturers.

Rep. Annual Meeting German Pulp and Paper Chemists (1911) p. 43.

Mitscherlich, A.—PROCESS FOR PREPARING EMULSIONS SUITABLE FOR PAPER SIZING.

Mixture of waste sulphite liquor with tannin glue or rosin glue and soda at 30° and 60°.

German Patent 220066 (1908).

Mitscherlich, A.—PROCESS FOR PREPARING EMULSIONS SUITABLE FOR PAPER SIZING.

A solution of horn in soda is mixed with sulphite waste liquor and the mixture precipitated with hydrochloric acid. The precipitate is washed out and dissolved in borax. Rosin size is added to this solution, whereby an emulsion is obtained which, diluted with water, can be precipitated with alum. The emulsion can also be precipitated with rock salt and the precipitated substance, which is nearly free from water, can be used as a "tannin size."

German Patent 235965 (1911) (addition to German Patent 220066).
Papier-Ztg. vol. 36 (1911) p. 2077.
Papier-Fabr. vol. 9 (1911) p. 825.
J. Soc. Chem. Ind. vol. 30 (1909) p. 1051.

Trainer, E.—ADHESIVE FROM WASTE SULPHITE LIQUOR.

The liquor coming from the digester is conducted to an electrolytic bath provided with diaphragms, where it is treated at the anode and the cathode alternately with a direct current of low voltage.

German Patent 239675 (1909).
Z. angew. Chem. vol. 24 (1912) p. 2335.
Chem. Abs. vol. 6 (1912) p. 2169.

Kausch.—ADHESIVES AND BINDING MATERIALS.

A review of patented uses of waste sulphite liquor.

Kunststoffe III (1913) pp. 112, 127.

Landmark, H. B.—UTILIZATION OF WASTE SULPHITE LIQUOR.

Norwegian Patent 21848 (1911).
(See "Alcohol" p. 105.)

Ellis, C.—CONCENTRATING WASTE SULPHITE LIQUOR FOR USE IN PAPER SIZING.

The liquor is heated to 40° C. and air blown through at a temperature of 60° to remove a portion of the free SO_2. The liquor is made alkaline with $Ca(OH)_2$ and heated to 60° with continued aeration, filtered, concentrated under reduced pressure, and the insoluble products removed.

United States Patent 1057416 (1913).
Chem. Abs. vol. 7 (1913) p. 1806.

Patch, F. H.—NEW ADHESIVE FROM WASTE SULPHITE LIQUOR.

Oil or fats prepared so they will mix with concentrated (1·3 to 1·4 sp. gr.) liquor and flour or other ingredients necessary to make the composition into a paste-like form, are added. May be used as paste or evaporated, whereby it may be adapted for the use intended.

Paper vol. 15 (1914) No. 11 p. 21.

DeCew, J. A.—ADHESIVE FROM WASTE SULPHITE LIQUOR.

Liquor concentrated in vacuo with an excess of magnesium oxide and magnesium chloride is added to the product in a proportion equivalent to the amount of magnesium oxide remaining in excess, to form magnesium oxychloride.

United States Patent 1203856 (1916).
J. Soc. Chem. Ind. vol. 35 (1916) p. 1257.
Chem. Abs. vol. 11 (1917) p. 100.
Paper Makers' Monthly J. vol. 54 (1916) p. 212.

Haeffner, A. H.—SIZING PAPER BY FERMENTED SULPHITE LIQUOR.

The fermented liquor, from which the alcohol may be distilled off, may be used directly or in addition to rosin size. 20 litres (4·4 gallons) of waste liquor of 10 per cent dry substance is equivalent to 1 kilogramme (2·2 lb.) rosin size. The alum is added approximately in the same proportion as with rosin size. For common wrapping paper the following mixture is found to be suitable. For 100 kilogrammes (220 lb.) paper, 25 kilogrammes (55 lb.) waste liquor of 10 per cent dry substance, 0·5 kilogrammes (1·1 lb.) rosin soap, 1·0 kilogramme (2·2 lb.) alum.

United States Patent 1231153 (1917).
Paper vol. 20 (1917) No. 21 p. 23.
Paper Making vol. 36 (1917) p. 238.
Pulp Paper Mag. Can. vol. 15 (1917) p. 1031.
Paper Makers' Monthly J. vol. 55 (1917) p. 277.

TANNING MATERIALS

In 1878 Mitscherlich obtained a German patent for a process for extracting tannin and other substances from oak with calcium-sulphite solutions at a temperature above 108° C., with the simultaneous production of cellulose and acetic acid as by-products. Since that time a great number of patents have been granted for methods utilizing waste liquor produced in the manufacture of sulphite pulp from coniferous woods, but no other questions in connection with this problem have been discussed with more interest and with more diversity of opinion than those regarding the suitability of the waste sulphite liquor for tanning purposes. It has, in fact, been doubted whether the liquor contains substances with tanning properties. The actual presence of tannin in the ordinary waste sulphite liquor has never been definitely proven, although it has been claimed by some investigators. Evidently the presence of tannin has in some cases been concluded from the fact that the waste sulphite liquor precipitates a glue solution and gives a faint colour reaction with iron solutions, both of which reactions are no doubt caused by certain substances very similar to tannin. Spruce wood contains some tannin which might pass into the liquor during the cooking process, but even assuming a tannin content of 3 per cent in spruce wood, which of course is a very high estimate, Landmark calculates a maximum tannin content of 0·6 per cent in the waste liquor, corresponding to about 2·4 per cent in the concentrated extract of 27° Bé. It is, however, very probable that the tannin originally present in the wood is decomposed at the high temperature of the cooking process. However, since it has been shown by experiments that a hide absorbs from a good "sulphite extract" as much as 23-25 per cent of substances which are able to transform the hide into a leather, it must be concluded that these substances do not originate with the tannin of the wood but consist mostly of the sulphonic acids of the lignin, the organic bodies which give the reactions with glue and iron solution.

The concentrated tanning extracts from sulphite liquor are placed on the market under various names such as "Fichtenholz," "spruce wood," "pine wood," "excelsior," "sulphite extract liquor," etc. The fact that the tanning extracts from sulphite liquor may be products of very different treatments may account for the diversity of opinion regarding their tanning qualities.

In preparing a tanning extract from waste sulphite liquor it is necessary to remove certain substances which are not desired in the ultimate product and also to concentrate the liquor to about 30° Bé. The free and loosely combined sulphurous acid may be removed by heating with or without the addition of sulphuric acid or may be precipitated with part of the lime, as calcium sulphite, by adding the required quantity of lime. The lime organically combined is usually removed by precipitation with sulphuric acid or a soluble sulphate. Oxalic acid is often recommended for the removal of the last traces of lime, or lactic acid is used since the calcium compound of lactic acid is found to have no injurious effect in the tanning process. In some cases lactic acid is even added to the purified extract in order to facilitate the process. If zinc dust and sulphuric acid are added to the liquor a discolouring effect is obtained.

Other processes for the preparation of a tanning material make use of the addition of the sesquioxide of aluminium and chromium or the heating of the liquor with cyanide of potassium or sodium and the precipitation of an organic cyanogen with an acid.

According to Byrom's patent the liquors are treated with phenols, amino compounds or naphtalene disulphonic acids or mixtures of these substances, or with the middle fraction or the heavy oil from the distillation of coal, whereupon a soluble, light, tanning extract is obtained.

The variety of the processes which will be noted in the following abstracts probably gives the best explanation of the different results arrived at by practical tanning tests. It is claimed that sulphite extract when used alone or in large quantity in mixture with other extracts gives only a leather of inferior quality, and it is probable that the sulphite extract when used alone will not give a satisfactory product, although it has been stated on the other hand that this extract alone, if it is properly prepared, will give a leather superior to both hemlock and oak leathers.

For a successful tannage it is desirable to have a certain proportion between the tanning materials and non-tannins, and it is therefore of advantage to mix extracts of different composition in order to obtain this proportion. The sulphite extract has a high percentage of non-tannins. It has therefore been successfully mixed with quebracho extract, which has a considerable proportion of tannins but a low non-tannin content. The sulphite extract appears to be a good solvent for the portions of the quebracho extract, which are soluble with difficulty, namely, the phlobaphenes, whereby a better utilization of the tannins is secured, but the greatest advantages of the employment of sulphite extract in mixture with other extracts are apparently an acceleration of the tanning process and a lighter colour of the leather. Landmark also claims a higher yield, that is a higher absorption (up to 18 per cent more), with mixtures of quebracho and sulphite extracts than with quebracho alone, and assuming a price of $0.18 per kilogramme for quebracho extract of 25°-26° Bé. and a price of $0.056 per kilogramme for sulphite of 27° Bé. and assuming, further, a mixture in the proportion 1:1 he arrives at a saving in tanning material of $5.11 per 100 kilogrammes of leather. According to a letter from Mr. Landmark the sulphite extract produced in Norway and put on the market under the name "Norego" is extensively used in Norway and Sweden, usually in admixture with quebracho extract to as high as 50 per cent, to the satisfaction of the tanners. Whenever the tanners have been opposed to the use of the sulphite extract it has been because the extract alone or added to another extract in a large proportion has caused a "tinniness" and brittleness in the final leather. But this is no doubt caused by the use of extracts not properly prepared and purified. Even small quantities of iron and lime (which should not be present in such quantities as to be detected in the extract) will have a decided detrimental effect upon the leather. A proper removal of these substances, therefore, is essential in the preparation of the extracts. The tanners admit that the sulphite extract is useful as a weighing material and as a substitute for molasses and dextrose, and has the same value as these substances. But, while the latter can be with comparative ease washed out of the leather with water, the substances of the sulphite extract are more intimately combined with the leather. In fact, the sulphite extract is in some cases so well fixed in the leather that it cannot be detected by methods based upon the extraction of the leather with water.

As there may still be many lower grades of sulphite extracts on the market it is very important to be able to detect their presence in mixture. Analytical methods for this purpose have often been discussed and rather complete abstracts of such discussions are included in this section.

Finally, a few tables taken from different authors serve to give comparisons of various commercial sulphite extracts. Eitner gives the comparative analysis of various extracts as follows:—

——	Hungarian Extract.	German Extract.	Excelsior Extract.
	%	%	%
Substances removed by hide powder	22·8	22·6	25·8
Substances not removed by hide powder	27·5	28·2	28·0
Water	49·6	49·0	46·2

Beveridge gives the following table:—

—	Sulphite Liquor Extract. (Spruce).	Sulphite Liquor Extract. (Hemlock).	Extracted from Hemlock Bark with Water.
	%	%	%
Moisture	41·34	47·93	54·24
Total solids	58·68	52·07	45·76
Soluble solids	58·61	51·93	41·93
Insoluble solids	0·07	0·14	3·83
Non-tannins	39·36	24·84	16·63
Specific gravity	1·290	1·269	1·215

If calculated on total solids the amount of tannin is respectively 32·80 per cent, 52·02 per cent and 55·29 per cent.

The following table is taken from Landmark's publication "Sulphite Liquor as a Tanning Material", and represents a comparison of various sulphite extracts with tannin extract obtained from spruce.

Spruce Bark.	Bé.	Tannins	Non-Tannins	Total Solids.	Insoluble.	Water.	Sugar.	Ash.
		%	%	%	%	%	%	%
Spruce Bark. Extract (Swedish).	24°	22·2	19·1	41·3	2·6	56·1	4·6	2·5
Hocklingsen[3]). Cellulose fabrik...	32°	20·6	31·1	51·7	0·0	48·3	2·4	13·8
Gewerkschaft "Pionier"	33°	25·8	27·4	53·2	0·0	46·8	8·0	8·5
Hansa[1]) Combined Fichtenholz extract	33°	29·0	31·3	60·3	0·1	39·6	11·6[4])	7·9
Hansa[1]) Combined Fichtenholz extract	27°	25·0	22·6	47·6	0·0	52·4	......	5·4
Owens Extract. David Owen & Son	34°	22·3	38·9	61·2	1·1	37·7	11·6[5])	7·6
Owens Extract 12/12/13 from Rink Brothers, London	33°	24·4	33·9	58·3	0·3	41·4	13·6[5])	7·6
American[2]). Sulphite-Extract	27·2°	30·2	16·3	46·5	0·1	53·4	3·8	3·9
Saxonia from Paul Golden & Co., sample 12/2/14	27°	24·7	20·1	44·8	0·0	55·2	3·9	5·3
Excelsior	31°	16·55	33·80	50·35	0·0	49·65	....	12·16
Hoesch	33°	28·39	20·13	48·52	4·63	46·85	......	5·60
Heymann	24°	14·65	24·46	39·11	0·0	49·65	......	5·85
Muskegon[6])	30°	30·73	19·50	50·23	4·63	46·85	....	2·0
Norego	33·7°	28·3	31·6	59·9	0·1	40·0	10·0	6·7
Norego	27°	24·21	20·42	44·63	0·0	55·37	......	2·91

[1]) Hansa is mixed with gambier.

[2]) The proportion between tanning and non-tanning substances show that the extract is mixed to a large extent with other vegetable extract. The sugar content also indicated this.

[3]) Hocklingsen analysed by the shaking method, the others by the filter method. The analysis of Hansa is given by the firm.

[4]) The sugar tested in a sample by H. Landmark.

[5]) The high sugar content originates with some colouring substances which are not precipitated by ead acetate.

[6])The proportion between tannins and non-tannins proves that the extract is not pure sulphite extract but is mixed with other extract.

Mitscherlich, A.—PROCESS FOR THE PREPARATION OF TANNIN FROM OAK.

Claims.—The process described for the extraction of tannin from oak depends on the use of calcium sulphite as the extracting agent.

German Patent 4178 (1878).
Saxon Patent 3912 (1875).

Mitscherlich, A.—INNOVATIONS IN THE PROCESS OF PRODUCING TANNING MATERIALS WITH THE PRODUCTION OF THE BY-PRODUCTS, CELLULOSE, GUMS, ACETIC ACID, AND CALCIUM BISULPHITE.

(a) Claims.—1. The preparation of tannin, adhesives, and a fermentable liquid through treatment of the wood with a solution of calcium sulphite at a temperature of over 108°, as well as the simultaneous production of cellulose and acetic acid as by-products of this process.

2. The preparation of a solution of calcium bisulphite by further use of the sulphur dioxide, which is driven off.

3. The direct application of the sulphurous acid liquid or the evaporated material or the decomposed calcium tannate as a tanning material. Importance is attached to the advantageous action of the sulphurous acid.

(b) Claims.—The preparation of tannin substance by treating wood with the solution of the calcium salt at a temperature of over 108°, as well as simultaneous production of acetic acid as a by-product in this process.

German Patent 4179 (1878).
(Addition to German Patent 4178). Addition to the process for producing tannin by using the by-products.
Ber. vol. 12 (1879) p. 395.
Kirchner, Zellulosefabrikation (1907) pp. 23, 25.

Mitscherlich, A.—COOKING OF WOOD WITH CALCIUM BISULPHITE, RECOVERING CELLULOSE, TANNING MATERIALS, GUMS, ACETIC ACID.

English Patent 1668 (1882).
J. Soc. Chem. Ind. vol. 2 (1883) p. 700.

Pictet, R. P. and Brelaz, G. H.—IMPROVEMENTS IN SULPHITE WOOD-PULP.

Cooking of wood with supersaturated solutions of sulphurous acid gas at a temperature below 100° C. in order to avoid the decomposition of the resinous and other encrusting matters in the wood. Recovering of SO_2 and preparation of gums, resin, tannin, alcohol, etc., from the waste liquor.

English Patent 9509 (1884).
J. Soc. Chem. Ind. vol. 4 (1885) p. 464.

W. (Anonymous).—WASTE SULPHITE LIQUOR.

Description of the methods given by Hammer, Lowenthal, Councler, and Schrader, for determination of tanning acid. Analysis of liquors by these methods made the presence of tannin seem probable.

Papier-Ztg. vol. 16 (1916) pp. 1446, 1447.

Mitscherlich, A.—PROCESS FOR UTILIZING THE LYES OF SULPHITE-CELLULOSE PRODUCTS OBTAINED IN SUCH PROCESS AND APPARATUS EMPLOYED FOR THAT PURPOSE.

The inventor claims a separation of the constituents of the lye of sulphite cellulose by osmose, in a special apparatus, and utilizes such constituents for a tanning material and a cementation material. He also obtains alcohol by fermenting a certain portion of the liquor and, further, obtains food for animals.

German Patent 72161 (1891).
English Patent 12927 (1893).
Ber. vol. 27 (1894) p. 149.
Papier-Ztg. vol. 18 (1893) p. 3222.
J. Soc. Chem. Ind. vol. 13 (1894) p. 834.

Opl. C.—PREPARATION OF SULPHITE-CELLULOSE LIQUORS FOR TANNING PURPOSES.

The crude sulphite-cellulose liquors are treated with caustic lime for the removal of calcium bisulphite, normal calcium sulphite being precipitated; or the SO_2 is liberated by the addition of sulphuric or hydrochloric acid and then expelled from the liquors by steam. In the liquors thus purified, metallic tannates, soluble in water, are formed by the addition of metallic sulphates such as aluminium sulphate, alum or ferrous sulphate, whilst calcium sulphate is precipitated. The solutions of metallic tannates thus obtained possess, it is stated, tanning powers which it is proposed to apply in the tannery.

German Patent 75351 (1893).
J. Soc. Chem. Ind. vol. 14 (1895) p. 976.

Mitscherlich, A.—PROCESS AND APPARATUS FOR UTILIZATION OF WASTE SULPHITE LIQUOR.

Austrian Privilegium 112 (1894).
(See "Gums, Adhesives, and Sizing Materials" p. 68.)

Blackman, B.—UTILIZATION OF LIQUOR.

The liquor is blown into large chambers which are evacuated. The free SO_2 is drawn off with a vacuum pump and used again. The last amounts are obtained by heating the liquids. The liquor is then worked up for use as a tanning material.

United States Patents 369836, 369530, 369634, 530635 (1895).
Papier-Ztg. vol. 20 (1895) part I p. 1376, part II p. 2152.

Ekman, C. D.—WASTE SULPHITE LIQUOR.

Review of methods for utilization. Mitscherlich method for using the waste liquor for tanning hides has had no success, due to the absence of tanning material in the liquor.

Papier-Ztg. vol. 21 (1896) part I pp. 2218, 2609, 3247.
J. Soc. Chem. Ind. vol. 15 (1896) p. 735.

Mitscherlich, A.—REPLY TO EKMAN'S REMARKS ON SULPHITE LIQUOR.

Preparation of tannin "Gerbleim" and "dextrine" are considered.

Papier-Ztg. vol. 21 (1896) pp. 2349, 2850.

Honig, M.—TANNIN EXTRACT FROM WASTE SULPHITE LIQUORS.

The lyes are neutralized with calcium carbonate or lime and the clear solution concentrated to 15°-18°Bé. They are then heated with sufficient sulphuric acid to combine with the lime present in the lye. After being concentrated up to 28°-30°Bé. in a vacuum pan, and clarified, the solution may be used as a tannin extract.

English Patent 18265 (1896).
J. Soc. Chem. Ind. vol. 15 (1896) p. 819.

Kempe, D.—PRODUCTION OF TANNINS.

The liquor is boiled with lime under pressure, is filtered, and the filtrate worked up into tannins by heating under high pressure with sulphates of the heavy metals.

Austrian Privilegium 3962 (1897).
Swedish Patent 8422 (1897).
Chem.-Ztg. vol. 22 (1898) p. 26.

Ziegler, A.—TANNING BY MEANS OF ALTERNATE TREATMENT WITH SULPHITE LIQUOR AND METALLIC SALTS.

The hide is first treated with sulphite liquor and then treated with a solution of an alkali chromate or an aqueous solution of a salt of Al, Fe, Cu, or Cr. The leather obtained by this treatment is better than that by mineral tannage alone.

German Patent 105669 (1897).
Chem.-Ztg. vol. 25 (1900) part I p. 154.

Honig, M.—TANNIN EXTRACT FROM WASTE SULPHITE LIQUOR.

After precipitation of the lime, volatile gases are driven off with steam, and the liquor is then evaporated in vacuo.

Russian Privilegium 953 (1898).
Chem.-Ztg. vol. 23 (1898) p. 319.

Honig, M.—TANNING EXTRACT FROM SULPHITE LIQUOR.

Zinc dust and sufficient H_2SO_4 to liberate the combined sulphurous and acetic acids are added to the liquor, which have the effect of decolorizing the liquor. After partial evaporation the liquor so treated can be used as a tanning extract.

German Patent 132224 (1901).
United States Patent 727798 (1903).
Austrian Patent 7325 (1901).
Papier-Ztg. vol. 27 (1902) part II p. 2162.
Chem. Zentr. (1902) part II p. 174.
J. Soc. Chem. Ind. vol. 22 (1903) p. 753.

Honig, M.—PREPARATION OF A TANNING EXTRACT.

The liquor is run into a battery of vessels provided with stirrers. These vessels are so arranged that each of them can be put into connection with the liquor reservoir and can also be emptied. The underlying idea is to prepare an extract such that the tannins and non-tannins are in such a relation as has been shown to be best in practice, i.e. 100 tannin to 85 non-tannin. In the liquor treated according to German Patent 132224 (1901) the ratio is 100-110. Accordingly extracts are added which are low in non-tannins, e.g. quebracho, mimosa, myrobalans. Quebracho is especially suitable on account of its cheapness and its ratio of 100 tannins to 8 non-tannins. For 100 kilogrammes of quebracho wood 1·67 cubic metres of liquor 6° Bé are used for extracting the tannin from the wood.

German Patent 152236.
Austrian Patent 12970 (1902).
Papier-Ztg. vol. 29 (1903) part II p. 2226.
Jahrb. Chem. Techn. (1904) part II p. 514.

Karr, O.—TANNING MATERIAL AND PULP FROM CHESTNUT, OAK AND SIMILAR TANNIN-CONTAINING WOODS.

United States Patent 762139.
Papier-Ztg. vol. 29 (1904) part II p. 2726.

Kumpfmiller, A.—PURIFICATION OF SULPHITE LIQUOR.

The hot liquor is evaporated in vacuo to 25° Bé., with rapid stirring. The acids harmful to leather are volatilized, and $CaSO_3$ is precipitated. This is filtered off. The lime still remaining is precipitated with oxalic acid. An excess of oxalic acid does no harm. The liquor is again filtered. This filtrate is rich in tanning and filling organic substances. No organic substance is precipitated by this method. The extract while having a higher specific gravity than tanning extracts has a lower viscosity. It is easily soluble in water; it is not decomposed in the pit; the pores of the skin are not clogged up. It can be mixed readily with other extracts.

German Patent 183415 (1905).
Jahrb. Chem. Techn. (1907) part II p. 503.
Chem. Zentr. (1907) part II p. 109.
Wochbl. Papierfabr. vol. 38 (1907) p. 1402.
Papier-Ztg. vol. 32 (1907) part I p. 2046.
Chem.-Ztg. vol. 31 (1907) Rep. p. 243.

Kumpfmiller, A.—

The liquor is first warmed and then sprayed continuously or intermittently into a chamber in which a strong vacuum is maintained. It is stated that the sulphur dioxide escapes from the small particles of liquor almost instantaneously and that the whole of the dissolved calcium sulphite separates, whilst the liquor itself is not discoloured.

German Patent 203648 (1906).
Chem. Zentr. (1908) part II p. 1834.
Papier-Ztg. vol. 33 (1908) part II p. 3564.
Chem.-Ztg. vol. 32 (1908) p. 1036.
Wochbl. Papierfabr. vol. 40 (1909) p. 260.
J. Soc. Chem. Ind. vol. 27 (1908) p. 1174.
Chem. Abs. vol. 3 (1909) p. 714.

Honig, M.—PROCESS FOR MANUFACTURE OF TANNIN EXTRACT.

The waste liquor is treated with zinc dust and sulphuric acid or a stronger acid (Patent 7325), and before concentration in vacuo is filtered through a tannin-containing material or cooked with such a material.

Austrian Patent 31862 (1906) (Addition to Austrian Patent 7325).

Kumpfmiller, A.—PURIFICATION OF WASTE SULPHITE LIQUOR.

Austrian Patent 40657 (1906).
German Patent 183415 (1905).
(See " Miscellaneous " p. 168.)

Paeszler.—METHOD FOR IDENTIFICATION OF VARIOUS KINDS OF TANNING MATERIAL AND TANNIN EXTRACTS.

It is desirable to find a method for identification of tannin extract from waste liquor in tannin extracts. Sulphite liquor extract alone is not regarded as a tanning material but only as a substitute for other extracts, and can very well be used in mixture with other extracts.

Chem.-Ztg. vol. 30 (1906) part II p. 1000.

Philippi, W. H.—UTILIZATION OF SULPHITE LIQUOR FOR TANNING.

The warm liquor from the digester is treated in the following proportions: 1 litre of the liquor is heated with sodium carbonate until the reaction is alkaline; usually 20-30 grammes are necessary. Twenty to thirty grammes of alum are now added and the liquor is filtered. The filtrate is used for tanning. It tans quickly and intensively. The hides are also preferably subjected to the action of dilute hydrochloric acid, either after or during the tanning process, in order to improve their colour.

German Patent 195643 (1904) and 211348 (1905).
French Patent 369608 (1906).
Chem. Zentr. (1908) part II p. 1232 (1909) part II p. 400.
Papier-Ztg. vol. 33 (1908) part I p. 1210, vol. 34 (1909) part II p. 2294.
Jahrb. Chem. Techn. (1908) part II p. 557.
J. Soc. Chem. Ind. vol. 26 (1907) p. 106.
Chem. Abs. vol. 3 (1909) p. 2640.

Kumpfmiller, A.—PURIFICATION OF SULPHITE LIQUOR.

According to the chief patent, after removal of most of the sulphurous acid by evaporation and separation of the calcium sulphite the remainder of the lime was precipitated by addition of oxalic acid. According to the present patent, their residual lime is converted by addition of a suitable acid. e.g. lactic acid, into a calcium salt which has no injurious action in the process in which the sulphite liquor is to be subsequently used.

German Patent 194872 (1906) Addition to German Patent 183415.
Chem. Zentr. (1908) part I p. 1118.
Papier-Ztg. vol. 33 (1908) part I p. 896.
Chem.-Ztg. vol. 32 (1908) Rep. p. 255.
Wochbl. Papierfabr. vol. 39 (1908) p. 1306.
J. Soc. Chem. Ind. vol. 27 (1908) p. 562.

Kumpfmiller, A.—PURIFICATION OF SULPHITE LYES FOR TANNING.

The lye is first freed from the main portion of the sulphurous acid and calcium sulphite it contains by heating or by treatment in vacuo. It is then treated with ozone, whereby the remainder of the sulphurous acid and calcium sulphite are converted into sulphuric acid and calcium sulphate respectively, the greater portion of the latter separating out. On now adding barium carbonate the dissolved sulphuric acid and sulphate are precipitated. The liquor thus purified is suitable for use as a tanning and filling for hides.

German Patent 207776 (1906).
Papier-Fabr. vol. 7 (1909) part I p. 293.
Papier-Ztg. vol. 32 (1907) part I p. 986.
J. Soc. Chem. Ind. vol. 28 (1909) p. 484.
Chem. Abs. vol. 3 (1909) p. 2072.

Kumpfmiller, A.—PURIFICATION OF WASTE SULPHITE LIQUOR.

The waste liquors from the manufacture of sulphite cellulose are freed from sulphurous acid and calcium sulphite by evaporation in a vacuum apparatus, and are then treated with a solution of alum. The precipitate produced is separated. The solution thus obtained is suitable for use as a filling material in tanning and leather dyeing.

German Patent 216284 (1907).
J. Soc. Chem. Ind. vol. 28 (1909) p. 1324.
Chem.-Ztg. vol. 33 (1909) Rep. p. 627.
Papier-Ztg. vol. 34 (1909) part II p. 3716.
Chem. Abs. vol. 4 (1910) p. 1114.

Stewart, D.—PROCESS FOR MANUFACTURING TANNIN DYES AND EXTRACTS.

Waste sulphite liquor with less than 6 per cent iron (as found in the ash) is used. The liquor is percolated with tannin-containing materials and after removal of precipitate evaporated in vacuo.

Austrian Patent 40528 (1907).
United States Patent 909343 (1909).
Chem.-Ztg. vol. 33 (1909) Rep. p. 175.

Little, A. D.—PROGRESS IN THE MANUFACTURE OF SULPHITE PULP IN 1906.

(See "General" p. 185.)

Tillberg, E. W.—PROCESS FOR OBTAINING TANNINS, ALCOHOL, AND CELLULOSE FROM WOOD.

Swedish Patent 25283 (1907).

Johnson, J. Y. (From J. S. Robeson).—PREPARATION OF A TANNING MATERIAL FROM WASTE SULPHITE LIQUOR.

The new product consists of a soluble compound of the sesquioxide of chromium and aluminium with the practically unchanged organic matters of sulphite cellulose liquor, and is prepared by treating the liquor with aluminium and chromium sesquioxide and an acid capable of precipitating mineral matter from such liquor and removing the precipitate thus formed. After standing some time, the liquor deposits a second precipitate of sulphur, which is also removed. The solution is then concentrated or evaporated to dryness. The product is stated to be useful as a tanning material.

English Patent 17956 (1908).
United States Patent 851378-851381 (1909).
Austrian Patent 42479 (1909).
Chem.-Ztg. vol. 31 (1907) Rep. p. 312.
Papier-Ztg. vol. 35 (1910) p. 300.
J. Soc. Chem. Ind. vol. 28 (1909) p. 1052.

Robeson, J. S.—TREATMENT OF HIDES AND SKINS.

The processes consist of: (1) the treatment of hides or skins with a tanning agent, followed by a bath containing sulphite liquor (see preceding abstracts), and finally bleaching with an acid or other bleaching agent; (2) the tannage of hides or skins by means of sulphite liquors and bleaching with an acid or other material; and (3) tanning the hides or skins in sulphite liquors and subsequently bleaching by the use of sulphuric acid and a salt which reacts with the acid to effect the bleaching.

English Patent 17958 (1908).
J. Soc. Chem. Ind. vol. 28 (1909) p. 1052.

Johnson, J. Y. (From J. S. Robeson).—TANNING HIDES AND SKINS.

The method consists of treating the hides and skins, in successive baths of increased concentration, with a liquor containing a compound of the sesquioxide of aluminium or other base with the practically unchanged organic matters of waste sulphite liquors (see preceding abstract). The tannage can be completed in this liquor or it can be finished by any of the ordinary tanning processes. The patent also covers the treatment of cotton, wool, and other fibrous materials with the same liquor.

English Patent 17957 (1908).
J. Soc. Chem. Ind. vol. 28 (1909) p. 1052.

Teas, W. H.—TREATMENT OF PARTIALLY-TANNED LEATHER, WITH SULPHITE LIQUOR.

The claims are for a process of filling leather consisting in treating the partially tanned product with waste sulphite cellulose lyes which have been concentrated till they have the specific gravity 1·10-1·35, the liquor being agitated during the treatment.

United States Patent 916057 (1909).
J. Soc. Chem. Ind. vol. 28 (1909) p. 432.

PURIFICATION OF WASTE LIQUOR.

Discussion of Kumpfmiller's process for preparation of tannin extract.
Papier-Fabr. vol. 7 (1909) p. 293.

Procter, H. R., and Hirst, S.—DETECTION OF SULPHITE-CELLULOSE LIQUORS IN TANNING EXTRACTS.

If attempts are made to tan with this extract alone it is difficult, if not impossible, to obtain a product which deserves the name of leather, the surface being apparently tanned while the interior remains raw and unaltered, and the hide dries horny and usually has an unsatisfactory colour. If, however, the hide be in the first instance partially tanned with some ordinary tanning material or if some other tanning extract be used in conjunction with the "pinewood extract", leathers are produced similar in appearance to those of ordinary tannages, as the "pinewood extract", appears capable of absorption, giving firmness and weight, although it probably contains no bodies analogous to the ordinary tannins. It may, therefore, ultimately become a useful addition to the tanner's resources, but while experiments with it were at first apparently successful as a weighing and solidifying tan, some constituent appeared to accumulate in the liquors which led ultimately to the production of brittle or tender leather. Whether this was due to mismanagement the writers cannot at the moment say, but so far as they are aware but little of the extract has been sold to tanners under its own name. It is, however, obviously a tempting material for the extract manufacturer, as considerable quantities can be added to tanning extracts without altering their appearance, and it shows a good percentage of tanning strength by ordinary method of analysis. It is therefore important in the interests of the tanner that means should be discovered for the detection and, if possible, the estimation of "pinewood extract" in the mixture, and a good deal of time has been devoted by the writers to the attempts to discover a satisfactory qualitative colour reaction, and it has been found that the following modification of the ordinary test for lignin with aniline and hydrochloric acid is very delicate and quite satisfactory. It was also found that the "tanning substance" of the "pinewood", while it was estimated as tannin by the ordinary hide-powder process, was only to a very small extent capable of reducing permanganate in the Lowenthal method, and therefore gave almost negative results in tanning, a "pinewood extract" showing about 25 per cent of matters absorbed by the hide being only equivalent by the Lowenthal method to about 4 per cent of gallotannic acid. This property of low oxidizability is not shared to nearly an equivalent extent by any ordinary tanning material, and, therefore, "pinewood extract" can be detected and even estimated approximately if present in considerable quantity, by comparison of the gravimetric and Lowenthal results.

J. Soc. Chem. Ind. vol. 28 (1909) p. 293.
Z. angew. Chem. vol. 32 (1909) p. 1566.
Chem. Abs. vol. 3 (1909) p. 2395.

Honig, M.—TANNIN EXTRACT FROM WASTE SULPHITE LIQUOR.

French Patent 413849 (1910).
Austrian Patent Application 3325 (1909).
Hungarian Patent Application 3806 (1910).
Chem.-Ztg. vol. 34 (1910) Rep. p. 251.
Z. angew. Chem. vol. 23 (1910)) p. 499.
J. Soc. Chem. Ind. vol. 29 (1910) p. 1121.

SULPHITE-CELLULOSE LIQUORS FOR TANNING.

Procter and Hirst's statements on "pinewood extract" are criticized as being based upon a superficial study of the subject. The defects in the leather they examined were probably due to lime. A cellulose extract properly freed from lime when used in combination, especially with natural quebracho, gives good leather.

Ledertechn. Rundschau. vol. 1 (1909) p. 361.
Chem. Abs. vol. 4 (1910) p. 3150.

Kumpfmiller, A.—TANNING COMPOSITION FROM WASTE SULPHITE LIQUOR.

The liquor is heated, poured into a vacuum chamber to free it from SO_2, concentrated and filtered to remove the precipitated $CaSO_3$, treated with Na_2CO_3 to convert $Ca(HSO_3)_2$ into $CaSO_3$ and Ca salts of organic acids into Na salts, filtered, treated with HCl, and combined with a fresh, vegetable, tannin-containing extract, as quebracho or mangrove extract, and a colouring material, as "leather-yellow".

United States Patent 939394 (1909).
Chem. Abs. vol. 4 (1910) p. 527.

Kumpfmiller, A.—PREPARATION OF TANNIN EXTRACT.

The lime in the concentrated liquor is precipitated with soda. The filtrate is treated with hydrochloric acid, further concentrated, and mixed with quebracho extract.

United States Patent 940394 (1909).
Papier-Ztg. vol. 35 (1910) p. 300.
Chem.-Ztg. vol. 33 (1909) Rep. p. 648.

Philippi, W. H.—WASTE SULPHITE LIQUOR FOR TANNING.

Austrian Patent Application 1821 (1909).
Chem.-Ztg. vol. 33 (1909) Rep. p. 447.

Honig, M.—TANNING EXTRACT FROM SULPHITE LYES.

The lye as obtained from the treatment of cellulose with calcium bisulphite is analysed; from the analysis is calculated the quantity of sulphuric acid necessary to decompose the esters and salts of sulphurous acid which are present and to partly liberate the sulphonic acids of lignin, present largely as calcium salts. After the addition of the sulphuric acid the solution is filtered through tanning material to remove iron, and then concentrated.

French Patent 413849 (1910).
J. Soc. Chem. Ind. vol. 29 (1910) p. 1121.

Kumpfmiller, A.—THE UTILIZATION OF WASTE SULPHITE LIQUOR IN THE TANNING INDUSTRY.

Discussion on evaporation of waste liquor, purification and preparation of " sulphite extract ". Difficulties in the manufacturing operation, and dangers in using lower grades of extracts. On the other hand there are advantages in using a mixture of good sulphite extract with quebracho extract.

Report on Annual Meeting of German Pulp and Paper Chemists 1910 p. 57.

Honig, M.—EXTRACT FOR USE IN TANNING.

The liquor is mixed with an acid (such as $H_2 SO_4$ forming an insoluble lime salt together with salts of such an acid in such proportion as appears necessary for freeing a portion of the ligninsulphonic acid and for converting the remaining lime salts into other readily soluble salts. Thereupon the product is filtered, if necessary, through a tanning material which forms insoluble compounds with iron, for the purpose of imparting to the final product certain definite tanning properties through the addition of a given proportion of sulphonic acids in free and combined state.

English Patent 7066 (1910).
Chem. Abs. vol. 5 (1911) p. 2989.

Kumpfmiller, A.—UTILIZATION OF SULPHITE LYES FOR TANNING.

According to the process described by the author the lyes are violently agitated whilst boiling, in order to eliminate a portion of the sulphuric acid. Sodium carbonate is then added and the sodium sulphite formed is converted into chloride by hydrochloric acid; lastly lactic acid is added, since the calcium lactate is not injurious in tanning. The purified lyes are evaporated in a vacuum circulation apparatus of the type used in the potash industry. It consists of an open boiler from which the lye circulates through a vacuum evaporating apparatus and back again to the boiler. The lyes contain 7-9 per cent of organic solids, including 2-3 per cent of tanning matter. In oak-bark extract the ratio of tanning matters to soluble non-tannins is 3 to 2, whilst in quebracho it is 20 to 1. By blending the wood extract with other tanning materials it is possible to prepare an extract very similar to oak-bark extract. The lyes must be thoroughly purified from lime and sulphurous acid, since these impurities would make the leather brittle and black. "Spruce wood" extract exerts a good mordanting action and yields a pale leather to which it imparts the necessary "handle", whilst the presence of the non-tannins gives body and weight. A combination of chrome and spruce extract tanning promises to become of very considerable importance in the near future.

Chem.-Ztg. vol. 34 (1910) p. 1352.
J. Soc. Chem. Ind. vol. 30 (1911) p. 19.
Chem. Abs. vol. 5 (1911) p. 2944.

DETECTION OF WOOD-PULP LIQUOR IN TANNING EXTRACTS.

When used alone the "sulphite extract" produces a very inferior leather, but it may be used to adulterate other extracts without causing any decided difference in the appearance of the leather. Procter and Hirst propose the following method of identification of sulphite extract in tanning extracts. When 0.5 c.c. of aniline is added to 5 c.c. of tanning extract a turbid emulsion is produced. In case of unadulterated extracts, the turbidity disappears on addition of 2 c.c. of concentrated HCl. If wood-pulp liquor is present a decided precipitation remains.

World's Paper Trade Rev. vol. 56 p. 390.
Chem. Abs. vol. 5 (1911) p. 3908.

Dickerson, W. H.—PROCESS FOR THE PRODUCTION OF TANNING AGENTS FROM WASTE SULPHITE LIQUORS.

Weakly acid or neutral reagents are used to liberate sulphurous acid from waste sulphite liquors, and tannin from the tannin complexes contained therein, without producing secondary decomposition of the resulting or remaining organic constituents. For example, oxalic acid, in the proportion of about one-half of 1 per cent to 1 per cent by weight, is added to undecomposed waste liquor, preferably immediately after its discharge from the digester and either in its untreated state or after free sulphur dioxide and calcium sulphite have been removed by evacuation, or by a stream of an indifferent gas, and preferably without any considerable concentration of the liquor. If complete removal of calcium is desired, sufficient oxalic acid must be added for this purpose. After settlement, the supernatant liquid is decanted off and immediately subjected to reduced pressure or to a stream of an indifferent gas to remove free sulphur dioxide, and this process may or may not be accompanied by concentration in a vacuum evaporator or otherwise. The liquors thus obtained may be used for leaching tannin-containing materials.

English Patent 7438 (1910)
J. Soc. Chem. Ind. vol. 30 (1911) p. 438.

Eitner, W.—TANNING EXTRACT FROM WASTE SULPHITE LIQUOR.

The extracts from waste sulphite liquor placed on the market under the name of "Fichtenholz" (spruce wood), "Excelsior" extract, etc., are very similar with regard to composition. They contain about 23 to 26 per cent of substances which are absorbed by the hide, and about 28 per cent which are not absorbed. The extracts contain no tannin but serve as a filler. They are good solvents for quebracho extracts which are soluble with difficulty due to the presence of free sulphurous acid, but they do not dissolve impure quebracho extracts perfectly. The addition of sulphite extracts accelerates the tanning process; the extracts serve as filler but they make the leather hard and brittle.

Gerber vol. 37 (1911) pp. 227, 241, 255.
J. Soc. Chem. Ind. vol. 30 (1911) p. 1269.

Platsch, M.—PROCESS FOR PURIFICATION OF WASTE SULPHITE LIQUOR BY PRECIPITATING THE INJURIOUS SUBSTANCES WITH CHEMICALS AT HIGH CONCENTRATION OF LIQUOR.

The precipitation is carried out after the removal of the acetic acid. In order to remove the sulphur the precipitation is carried out with salts, the bases of which either form no compound or easily decomposed compounds.

German Patent Application 26575 (1911).

Platsch, M.—PROCESS FOR PURIFICATION OF WASTE SULPHITE LIQUOR.

The lime is precipitated from the concentrated liquor with sulphuric acid, and the excess of acid removed with barium carbonate.

German Patent Application 26960 (1911).

Landmark, H. B.—UTILIZATION OF WASTE SULPHITE LIQUOR.

The liquor is evaporated with an acid forming insoluble calcium salts until all the lime is precipitated. Starch products are thereby inverted into fermentable sugars. The excess of acid is precipitated in form of an insoluble salt and the filtrate concentrated. The extracts can be used as an adhesive or tanning material.

Norwegian Patent 21848 (1911).
Swedish Patent 35500 (1911).
Ledertechn. Rundschau vol. 4 (1912) p. 308.
Papier-Ztg. vol. 36 (1911) p. 3706, vol. 38 (1913) p. 3063.
Chem. Abs. vol. 8 (1914) p. 2278.
Paper vol. 13 (1913) No. 11 p. 23.

Loveland, F. M.—ANALYSIS OF SULPHITE EXTRACTS.

J. Am. Leather Chem. Assoc. vol. 7 (1912) p. 368.

Sindall, R. W.—WASTE SULPHITE LIQUOR FOR TANNING PURPOSES.

The liquor is treated with aluminium or chromium salts, filtered, and afterwards evaporated to 31°-32°Bé. (specific gravity 1·275-1·285). The extract contains 22 per cent tanning and 32 per cent soluble non-tanning substances, 2 per cent insoluble non-tanning substances, and 4-8 per cent ash. Used alone the extract gives only leather of inferior grade; in mixture with genuine tanning extracts it is to a certain extent useful. Aniline and hydrochloric acid give with genuine extracts a clear solution, with sulphite extract a precipitate.

Paper Makers' Monthly J. vol. 39 (1911) p. 401.
Papier-Ztg. vol. 36 (1912) p. 300.
Pulp Paper Mag. Can. vol. 10 (1912) p. 59.

Claflin, A. A.—THE TANNING PROPERTIES OF WASTE SULPHITE LIQUORS.

The partly purified liquors were first suggested as a substitute for lactic acid in the tanning industry. This was a failure but it was discovered that the liquors contained considerable amounts of material absorbable by hide. The author claims that if the extracts are properly purified they have a distinct property of converting hide into saleable leather. He contradicts Eitner's assertion that the tanning properties are due to zinc sulphite since Amercan extracts do not contain this.

J. Am. Leather Chem. Assoc. vol. 7 (1912) p. 154.
Z. angew Chem. (1912) p. 1932.
Chem. Abs. vol. 6 (1912) p. 1383.

Sody, L.—TANNING EXTRACT FROM SULPHITE LYE.

Cellulose extracts when examined by Procter's filter-bell method show from 20 to 30 per cent of tannin and from 20 to 37 per cent of non-tannins, but with Lowenthal's permanganate method the figure for tannin is only about one-sixth as high. For the detection of cellulose extract in genuine tanning extracts, the author has found the most satisfactory the permanganate titration method and the aniline test recommended by Procter (J. Soc. Chem. Ind.). The loss of tannin, as indicated by the hide-powder method, when cellulose extract is mixed with a tanning extract, is confirmed (See Yocum and Faust). Comparative tanning tests were made with quebracho extract, cellulose extract ,and mixtures of the two, strips of hide being placed in the liquors and standing for some hours, being shaken for 30 hours, then washed and soaked in water for 15 minutes. At this stage all the samples appeared completely tanned, but after smoothing, lightly oiling on the grain and drying, it was found, on examining cut sections, that only the piece treated with quebracho extract had been properly tanned; all the other pieces showed a distinct line in the middle which was more pronounced the higher the proportion of cellulose extract employed. Moreover, in proportion as the relative amount of non-tannins in the extract was increased by addition of cellulose extract, the "rendement" or yield of leather decreased. The author considers that the addition of cellulose extract has a deleterious effect on drum tannage with other extracts. In vat tannage the cellulose extract may give rise to the acids necessary for the plumping of the hides, but through weakening of the liquors may diminish the yield of leather. Cellulose extracts may be used for the retanning of leather in place of extracts such as cutch and gambier, and may advantageously replace glucose and molasses. It is also useful for correcting the disagreeable brown colour imparted to leather by quebracho, mangrove, and divi-divi, but the retanned leather should not be exposed to light during drying, as this darkens the colour.

Chem.-Ztg. vol. 37 (1913) p. 442.
Collegium (1912) p. 529.
J. Am. Leather Chem. Assoc. vol. 7 (1912) p. 373.
J. Soc. Chem. Ind. vol. 31 (1912) p. 737.

Gross, F. F.—PROCESS FOR PREPARATION OF TANNING EXTRACT FROM WASTE SULPHITE LIQUOR.

Hydrochloric acid and sulphuric acid is added to the hot liquor and the rest of the lime precipitated with chromate of potassium. The liquor is concentrated to 20° Bé. and cooled under aeration. The precipitates are filtered off and the filtrate further evaporated.

German Patent Application G. 38003 (1912).

Honig, M.—PREPARATION OF A TANNING EXTRACT FROM WASTE SULPHITE LIQUOR.

So much sulphuric or oxalic acid is added that the total ligno-sulphuric acids contained in the liquor are set free and the total lime precipitated.

German Patent Application H. 56968 Cl. 28a (1912).
Austrian Application A. 1511. (Addition to Patent 43742).

Paeszler.—TANNING EXTRACTS ADULTERATED WITH CELLULOSE EXTRACT.

In the author's experience no leather of any value can be made by the use of cellulose extract alone. In one case, in which the tanning was allowed to proceed for a year, a kind of leather was produced, but its character was unsatisfactory and the gain of weight very small. When cellulose extract is used mixed with other extracts, good leather is obtained but it is difficult to see whether the action is due to the other materials alone or whether the cellulose extract plays any part. It is quite possible that the latter may have certain tanning properties of its own when mixed with other extracts. Procter and Hirst's lignin test gives a negative result with an extract made by treating quebracho wood for 12 hours at 2 atmospheres pressure without bisulphite or for 5 hours at 2 atmospheres pressure with 4 per cent of bisulphite. When the latter treatment is carried out at 6 atmospheres pressure a positive result is obtained but these conditions are never present in manufacturing. In the discussion it is stated that abnormal results were obtained in the examination of oak-wood extract when bad or spoiled wood had been used for its manufacture. Large quantities of cellulose extract are used in leather manufacture in England. A marketable leather can be produced by using a mixture of mangrove and cellulose extract in the proportion of 2 to 1.

Chem.-Ztg. vol. 36 (1912) p. 812.
J. Soc. Chem. Ind. vol. 31 (1912) p. 736.

Paeszler.—THE SUGAR CONTENT OF VEGETABLE TANNING MATERIALS AND TANNING EXTRACTS.

Ledertechn. Rundschau. vol. 4 (1912) No. 46-48.
Deut. Gerber Ztg. (1912) No. 55.
Collegium (1913) p. 88.

Bennett, H. G.—WOOD-PULP AND TANNING EXTRACTS.

The by-products from the pulp manufacture sold as vegetable tanning agents apparently contain a considerable amount of tannin when analysed by the official methods. However these so-called "pinewood" or "spruce" extracts answer only a part of the tests for tannin and do not contain true tannic acid. Tests proving this are mentioned. Also, tests for sulphite extract are given. The author has been discouraged by attempts, which he has seen, to make leather by using wood-pulp extracts. The product has a surface apparently tanned while the interior is unaltered and the hide is horny and not satisfactory in colour. Hides partially tanned with some ordinary tanning extract are similar in appearance to leathers of ordinary tannages. Evidently wood-pulp extracts are of use only in adding weight and as such have their risks.

Shoe and Leather Rep. vol. 104 (1912) No. 3, p. 31.
Chem. Abs. vol. 6 (1912) p. 1383

Chemische Industrie-und Handels-Ges. M. H.—TANNING PROCESS WITH WASTE SULPHITE LYES.

In the use of waste sulphite lyes for tanning, claim is made for the addition of glycerin as well as of chromium compounds. The chromium compounds diminish the solubility of some of the organic constituents of the liquors, and hence prevent to some extent their removal from the hide by washing. By the addition of glycerin, the possibility of concentrating the liquors to the desired extent whilst still maintaining them in the liquid state is achieved.

German Patent 248055 (1910).
J. Soc. Chem. Ind. vol. 31 (1912) p. 999.

Philippi, W. H.—TANNING EXTRACT FROM SULPHITE LYES.

The claim is for the addition of chromium hydroxide to the extract for the purpose of neutralizing any acid liberated during the tanning process.

German Patent 254866 (1910).
French Patent 448064 (1912).
Papier-Fabr. vol. 11 (1913) p. 102.
J. Soc. Chem. Ind. vol. 32 (1913) pp. 438 and 439.

Parker, J. G.—WASTE SULPHITE LIQUOR AND ITS USE IN THE LEATHER INDUSTRY.

Some investigators deny the tanning quality of the sulphite extract. Previous to and after tanning with pure extract treatment with sulphite extract in intervals is proposed. The extract could be used as a loading material in place of molasses, starch, sugar, etc. It is also proposed to study only the liquor from the first stage of the cooking process for tanning purposes. The aniline test is not decisive, as other substances extracted from the wood give this reaction.

Report 11. Ann. Meeting of I.V.L.J.C.
Collegium (1912) p. 611.
Chem.-Ztg. vol. 37 (1913) p. 6.
Chem. Abs. vol. 8 (1914) 839.

Yocum, J. H. and Faust, A.—USE OF SULPHITE-CELLULOSE EXTRACTS FOR BLENDING.

The use of sulphite-cellulose liquors for tanning has hitherto not met with much success, for if used in too great concentration the resulting leather often has a "tinny" feeling and a harsh grain. On blending the sulphite cellulose extract with other extracts, difficulties have also been met with because of the different behaviour with the different materials. The object of the present work was to determine the best conditions and the most suitable materials to blend with the cellulose liquors. A commercial sulphite-cellulose extract was used in the experiments. With every material which was tried, with the exception of the liquid quebracho extract, there was a loss of tannin produced by mixing. Mixtures of mangrove cutch with sulphite cellulose show no loss until more than 30 per cent of sulphite cellulose extract is used in the mixtures. In most cases the greater the amount of sulphite cellulose extract present, the greater the loss. With a mixture of equal parts of chestnut and cellulose extracts the loss was 6 per cent. With a similar mixture containing myrobalans the loss was 3-4 per cent. The losses with valonia are not quite so high as with myrobalans. With more than 30 per cent of the cellulose extract the resulting leather had a "tinny" feeling.

J. Am. Leather Chem. Assoc. vol. 6 (1911) p. 537.
J. Soc. Chem. Ind. vol 31 (1912) p. 36.
Collegium (1912) p. 227.
Chem.-Ztg. vol. 37 (1913) Rep. p. 115.

International Association of Leather Trade Chemists.—DETERMINATION OF TANNING MATERIAL.

Gravimetric determination of tannins and non-tanning substances by the method of the International Association of Leathern Trade Chemists; filter method and the jarfiller method by Procter.

Chem. Techn. Neuzeit O. Dammer.
Enke, Stuttgart, vol. 1 (1910) p. 689 vol. 3 (1911) p. 15 (Tanning materials from Sulphite liquor).

Grosser, G.—SULPHITE EXTRACT.

The analysis of Honig's extract gave 23 per cent tanning substances, 30 per cent soluble non-tanning substances, and 4·3 per cent ash. In spite of 0·6 per cent of SO_2 the extract mixes with any other extract without precipitation. It is not suitable for after-tanning or loading, but for pre-tanning.

In qualitative reactions for detection of adulterations the behaviour towards bromine water on one hand and formalin hydrochloric acid on the other hand are especially recommended; further the behaviour towards ferroatum and aniline hydrochloric acid. The SO_2 content and the ash content are particularly decisive.

Technikum vol 20 (1912) p. 156.
Chem.-Ztg. vol. 37 (1913) Rep. p. 442.
Collegium (1912) pp. 510, 557.

Grosser, G.—THE PHLOBAPHENE DISSOLVING PROPERTY OF NERADOL D. IN MIXTURE WITH QUEBRACHO-SULPHITE EXTRACT.

Sulphite extract causes a precipitate with all tanning substances, and only with quebracho extract does it cause an increase in tanning substances, on account of its property of dissolving phlobaphene. If, however, the quebracho-sulphite-extract mixture is mixed with other tanning materials the unchanged sulphite extract precipitates the foreign tanning substances. If the precipitate is dissolved by the addition of 50 per cent Neradol D. the total amount of tanning substance is increased. Neradol makes any precipitation of tanning material impossible.

Collegium (1913) p. 479.

Franke, H.—VEGETABLE TANNING MATERIALS.

Occurrence, qualities, preparation, and uses of the most important vegetable tanning materials.

Magdeburg (1909.)

Schneider, F.—UTILIZATION OF THE LIQUORS FROM THE FIRST STAGE OF THE SULPHITE PROCESS.

The observer is recommended to study the first extracts in the sulphite process (See also Ziegler).

Collegium (1912) No. 512 p. 678.

Gansser, A.—DETECTION OF WASTE LIQUOR IN LEATHER.

Pieces of ox hide are tanned with a dye (solution) containing 2-5 per cent waste liquor. The leather is afterwards extracted and the extracts compared tintometrically for intensity of colour with a 1.2 per cent tanning solution, as suggested by Procter and Hirst. In the case when 5 per cent waste liquor was used a certain quantity of the dilute solution gave the characteristic reaction (flakes at once) when 5 c.c. aniline and afterwards 20 c.c. concentrated hydrochloric acid were added. When 2 per cent was used the reaction took place in a few minutes.

Collegium (1909) p. 360 (1912) p. 482.
Z. angew. Chem. vol. 26 (1913) p. 528.
Chem.-Ztg. vol. 37 (1913) Rep. p. 442

Winter, H,—ACTION OF THE CELLULOSE TANNING EXTRACT UPON QUEBRACHO EXTRACT.

Contrary to several leather chemists the author states that an increase of tanning substance is secured when cellulose extract is added to solid Argentine quebracho extract, especially at 100°C. Perfect solubility in the cold is only obtained when pressure is used.

Ledertechn. Rundschau. vol. 5 (1913) p. 161.
Z. angew. Chem. vol. 26 (1913) p. 646.

Dickerson, W. H.—PROCESS OF TREATING WASTE SULPHITE LIQUOR FOR THE MANUFACTURE OF TANNING EXTRACTS.

In the manufacture of tanning extracts from waste sulphite liquor the latter is digested with an electrolyte such as sodium chloride, capable of gelatinizing the liquor or of converting it into a light-coloured mass of thin consistency when concentrated. To this mass may be added a thin tanning extract made by the addition to waste sulphite liquor of a non-decomposing "precipitant" for lime.

United States Patent 1043303 (1912).
Paper Trade J. vol. 57 (1913) No. 2 p. 42.
Schwalbe Lit. (1913).
Wochbl. Papierfabr. vol. 44 (1912) p. 4796.
J. Soc. Chem. Ind. vol. 31 (1912) p. 1140.

Platsch, M.—PRECIPITATION OF OBJECTIONABLE CONSTITUENTS OF SULPHITE LYE.

The precipitation of the calcium salts as sulphate can be completely effected only after elimination of the volatile organic acids (acetic acid) by evaporation of the lyes to a syrupy consistency. The reagents then used must be such that their bases form with sulphurous acid readily decomposable compounds only, or else do not combine at all. Aluminium sulphate, for instance, would be suitable, but precipitation may equally well be effected by sulphuric acid, provided the liquor be neutralized after the separation of the precipitate of calcium sulphate.

French Patent 447578 (1912).
United States Patent 1054141 (1913).
J. Soc. Chem. Ind. vol. 32 (1913) p. 284.

Gianoli, G.—PROCESS OF PRODUCING TANNING EXTRACT.

Crude, resinous, quebracho extracts are rendered soluble by treatment at 95°—115°C., with a solution of sodium lignosulphonate, obtained, for example, from waste liquor from sulphite-pulp making by treatment with lime water to remove sulphurous acid, followed by sodium sulphate to remove excess of lime.

United States Patent 1063428 (1913).
J. Soc. Chem. Ind. vol. 32 (1913) p. 760.

Auerbach, J.—IDENTIFICATION OF SULPHITE EXTRACT IN TANNIN EXTRACTS.

The Procter-Hirst reaction can also be obtained when sulphite extract is not present. Only a negative reaction, therefore, is decisive. The Lowenthal-Procter method for determination of the tanning value is important.

Chem.-Ztg. vol. 37 (1913) p. 906.

Albersheim, M.—PROCESS FOR PREPARATION OF TANNIN EXTRACTS FROM WASTE SULPHITE LIQUORS.

An acetate, especially sodium and ammonium acetate, is added to the sulphite liquor and the mixture heated for a certain length of time, whereby the iron is precipitated. The filtrate may be treated with ammonia and carbon dioxide in order to remove the rest of the lime present.

German Patent Application A. 22952 (1912).

Moeller, W.—NERADOL TANNING SUBSTANCE.

Discussion of the behaviour of the sulphite extract with Lowenthal's method of testing (permanganate) and the possibility of precipitation with hydrochloric acid and aniline.

Collegium (1913) p. 489.

Monnet C.—SULPHITE EXTRACT IN TANNING EXTRACTS.

The Procter-Hirst method for detecting sulphite extract is not reliable.

Collegium (1913) p. 224.
Z. angew. Chem. vol. 31 (1913) p. 646.
Chem. Abs. vol. 7 (1913) p. 3856.

Jedlica, F.—WASTE LIQUOR IN THE TANNIN EXTRACTS.

In using more than 5 c.c. oak-extract solution sulphite extract could be detected with certainty with the Procter-Hirst reaction (0·5 c.c. water-white aniline, and 2 c.c. concentrated hydrochloric acid). If no distinct formation of flakes takes place after two hours in oak extract the extract is free from sulphite extract.

Collegium (1913) p. 317.

Sommerhof, E. O.—RENDERING TANNING EXTRACTS SOLUBLE WITH SUGAR AND SODIUM BISULPHITE.

The tanning effect of the sulphite extracts is based partly on the effect of the colloidal sulphur.

Collegium (1913) p. 489.

Stutzer, A.—PROCESS FOR INCREASING THE AMOUNT OF TANNING SUBSTANCE IN THE SULPHITE EXTRACT.

Lactic acid is added to the lime—free liquor before, during or after the evaporation, in such a quantity that 10-50 parts lactic acid are used to 100 parts dry substance of the cooking liquor. The lactic acid or part of it may be produced in the waste liquor.

German Patent Application St. 18199 (1913).

Stutzer, A.—PREPARATION OF TANNING MATERIAL FROM WASTE SULPHITE LIQUOR.

The lime is removed with ammonium sulphate.

German Patent Application St. 17977 (1912).

Luhrs, O.—PROCESS FOR PREPARING A DECOLORIZED, COMMERCIAL, LIME-FREE TANNIN EXTRACT FROM WASTE SULPHITE LIQUOR.

Sodium bicarbonate or potassium bicarbonate, alone or in mixture with ammonia and phosphoric acid, is used for precipitating the lime.

German Patent Application L. 34995 (1912).

Stutzer, A.—CONTENT OF TANNING SUBSTANCES IN WASTE SULPHITE LIQUOR.

For removing calcium compounds from the lye, the addition of ammonium sulphate before concentrating is recommended. In this way, it is possible to obtain a liquor of 30° Bé (specific gravity 1.262) containing only 0.08 per cent CaO and 0.84 per cent of mineral matter. The content of tanning substances (substances absorbed by hide powder) in the lye can be increased by the addition of different substances (sodium sulphate and bisulphate; salts of aluminium, zinc, iron, manganese, and chromium; phosphoric, acetic, and lactic acids). For example, an addition of 50 grammes of 74 per cent lactic acid (per litre of original lye) to a lye to which 30 grammes of ammonium sulphate had been added before concentrating to 30° Bé., the content of tanning substances rose from 49.65 to 62.9 per cent. The leather produced by the concentrated liquor was of a light colour.

Z. angew. Chem. vol. 26 (1913) p. 463.
Wochbl. Papierfabr. vol. 44 (1913) p. 3339.
J. Soc. Chem. Ind. vol. 32 (1913) p. 8877.
J. Am. Leather Chem. Assoc. vol. 8 (1913) No. 11, p. 481.

Abraham, F.—ACTION OF LACTIC ACID ON SULPHITE-CELLULOSE LYE.

The author shows that the analysis of sulphite-cellulose liquors by the "filter-bell" method presents difficulties not experienced with the ordinary tanning extracts. Variations in the strength of the liquor for analysis have a great effect on the results of analysis, and the author recommends that solutions of sulphite cellulose for analysis should be of a concentration corresponding to 3.5 grammes of tannin per litre. The use of lactic acid for swelling hide is known, and the increased tanning effect observed by Stutzer on adding lactic acid to sulphite-cellulose extract is considered to be due entirely to the hide powder becoming swollen by the acid and thus acquiring greater absorptive power for tannin.

Gerberei-Technik (1913) Nos. 11, 12.
Collegium (1913) 11,599.
J. Soc. Chem. Ind. vol. 32 (1913) p. 1079.

Eitner, W.—CELLULOSE EXTRACT.

Practical tests of cellulose extract have established the fact that it is not an actual tanning material and has not the property of converting hide into a commercial leather. Hide treated with cellulose extract cannot be reconverted to raw skin by simple washing; a colouration is produced completely through the skin and, when dried out, the skin is less transparent than is raw hide but is as hard and stiff as the latter. A rational analysis of cellulose extract should consist in estimating its total solid matter and mineral matter. From the former an estimate of its value as a filling material can be made and from the latter an idea of how far it has been purified from materials injurious to the leather. The cellulose extracts formerly on the market contained 50 per cent of solid matter and 5-8 per cent of mineral matter, resembling in this respect sulphited quebracho extracts. The use of cellulose extract as an adulterant of tanning extracts has reached large dimensions. Cellulose extract is added to other extracts not only to lessen the cost but also because it confers a better appearence on an inferior extract and improves its solubility. Beside the aniline hydrochloride reaction for cellulose extract (J. Soc. Chem. Ind. vol. 28 (1909) p. 293) its presence may be detected by the proportion between "matter absorbed by hide" and "non-absorbed", which in the case of this material is about 1:0.82. For some other extracts the proportion is as follows: Quebracho extract 1:10; oak-wood extract 1:23; chestnut-wood extract 1:30; and myrobalans 1:215. The high ash content of cellulose extract (up to 9 per cent) is also found in some strongly sulphited tannin extracts, so a high percentage of ash need not necessarily imply its presence. Yocum has shown that by admixture of cellulose extract with tanning extracts a loss of tannin occurs which increases as the proportion of the former is increased; solid quebracho extract loses 4 per cent of tannin; catechu, 7 per cent; and chestnut extract 6 per cent. The author has shown that by treating the residue, obtained after allowing a solution of Argentine extract to settle, with sulphite liquor of 7° Bé. (specific gravity 1·05) an increase of 3 per cent of matter absorbed by hide in the extract is obtained. Grosser has shown that by treatment of already tanned leather with sulphite cellulose a dark colouration is produced in the liquor, caused by the removal of tannin or colouring matter, from the leather, while the colour of the leather is improved. By treatment with sulphite-cellulose liquor, only the "difficultly-soluble" and not the "insoluble" portions of quebracho extract are brought into solution. This solution cannot be ascribed to the sulphites in the cellulose liquor, as the purified extract has also the solvent action. The explanation probably lies in the fact that the "difficultly-soluble" tannins dissolve more readily in a tannin solution than in water. As a material for filling and adding weight the cellulose liquor is applied either like glucose to the tanned and struck-out leather or the dried or well-pressed leather is hung in a strong solution. The liquor penetrates and fills the leather more quickly in the latter way than does a tannin solution which is usually employed for that purpose, but for that reason it does not add much weight to the leather. Cellulose extract may be incorporated with leather in much larger quantities than can a tanning extract, but a limit is reached at which the leather becomes brittle. The high solubility of cellulose extract may cause stains to appear on the leather which has been treated with it and the surface of which has been washed with water to improve the colour, the extract dissolving from the centre of the leather and not merely from the surface. The brittleness of leather heavily loaded with cellulose extract may be lessened by incorporating the latter with a fatty material in a fine state of division, the acid oleates being the most suitable fats. The fat may cause a darkening of the colour of the leather and must be removed from the surface by treatment with soda and acids. The use of cellulose extract during the actual tanning process presents greater difficulties. The author has shown that the addition of the extract to the liquors, making the density greater, considerably hastens their tanning action. The rate of diffusion is increased by the increase in their density, and the penetration of tannin to the interior of the hide is hastened without any objectionable consequences such as drawn grain. Attempts have been made to produce the same effect by adding neutral salts such as sodium chloride and potassium sulphate to the liquors, but these have the disadvantage that tannin is precipitated by them from the liquors. The addition of cellulose extract to other extracts, where it would improve them, should be made in the hot condition, and 20 per cent should be sufficient to produce the best results. By the addition of 20-30 per cent of cellulose extract 2-5 per cent of the time necessary for the tanning process is saved. It will be found that cellulose extract must become much cheaper than at present if it is to find a use in this connection.

Gerber vol. 39 (1913) pp. 43, 57.
J. Soc. Chem. Ind. vol. 32 (1913) p. 229.

Hurt, H. H.—TANNING COMPOUNDS FROM SULPHITE LIQUOR.

A tanning composition is made by treating the waste lyes with a salt of a sesquioxide combined with an acid capable of forming insoluble calcium salts and removing the insoluble calcium salt formed. The resulting solution containing the organic matters of the wood-liquor substantially in their original relative ratios and composition is substantially free from lime, and contains alumina or other sesquioxide base in amount equivalent to the lime in the original liquor.

United States Patent 1075916 (1913).
J. Soc. Chem. Ind. vol. 32 (1913) p. 1079.
Chem. Abs. vol. 7 (1913) p. 4095
Paper Trade J. vol. 58 (1913) No. 44 p. 44.

Walker, W. O.—THE PROBLEM OF THE WASTE LIQUORS FROM SULPHITE PULP-MILLS.

"R. T. Mohan investigated the subject of tanning and found that the addition of lactic acid to the liquor improved the tanning properties. He tried the effect of the addition of sulphites and acids on ordinary hemlock-bark liquor, finding that they caused swelling, bleaching, and hardening of the leather. He also tried the effect of an addition of sulphites to waste sulphite liquor and found swelling, hardening, and bleaching to occur. He removed the lime and found very little difference in quality of the leather. Removal of the gummy matters destroyed all tanning property, further, the gums when redissolved would not tan. However, the addition of lactic acid improved the tanning markedly. During this work it was noticed that, according to the different percentages of acid in the liquor, the leathers varied from hard and bleached to black and flabby. Experiments were carried out to determine what relation of tannin to acid was best to produce leather of a good colour and texture. It was found that each acid has a factor for each tanning extract. With bark liquors the best ratio was found to be 0·8 (tans 8° acid 10) for lactic acid. For sulphite liquors the ratio was 1. For equal parts of sulphite liquor (spruce) and quebracho the ratio was 0·4. From this it would seem, therefore, that for heavy leathers, when acidity of liquor is needed, more uniform and reliable results could be obtained by the proper control of the ratio of acid to tannin in the first half-dozen vat liquors at least."

J. Soc. Chem. Ind. vol. 32 (1913) p. 389.
Chem. Eng. vol. 17 (1916) 246.
Paper vol. 11 (1913) No. 9 p. 21.
See " General " p. 185.)

Monnet, C.—SULPHITE-CELLULOSE LIQUORS IN TANNING EXTRACTS.

At the last conference in London of the International Association of Leather-Trades Chemists it was decided that the presence of a "pseudo-tannin" (e.g. sulphite-cellulose liquor) when detected in an extract should be mentioned in the report of the analysis. The author points out that Procter and Hirst's aniline-hydrochloride test has lately been found to give rise to erroneous deductions and to give varying results in the hands of different observers, and its indication should therefore be confirmed by other reactions.

Collegium (1913) p. 224.
J. Soc. Chem. Ind. vol. 32 (1913) p. 616.

Loveland, F. M.—DETECTION OF SULPHITE-CELLULOSE EXTRACT.

Gansser has stated that leather tanned in extracts containing 2-5 per cent of sulphite cellulose will give an extract yielding the characteristic flocculent precipitate, on treatment with aniline and hydrochloric acid. The author was unable to obtain the test with leather tanned in sulphite-cellulose extract alone, in liquors as high as 50° Bé. It appears that different sulphite-cellulose extracts give results at variance by the same tests, or else the extract changes during the process of leather manufacture. The heavy white precipitate which settles out of certain classes of sulphite-cellulose extract consists of sulphur.

J. Am. Leather Chem. Assoc. vol. 8 (1913) p. 128.
J. Soc. Chem. Ind. vol. 32 (1913) p. 373.

Small, F. H.—REPORT OF COMMITTEE ON ANALYSIS OF SULPHITE-CELLULOSE EXTRACTS.

There is no really trustworthy method of estimating the amount of tannin in an extract due to the addition of sulphite extract. The substance in sulphite extract which exercises a tanning effect on hides has a lesser effect compared to true tanning liquors.

J. Am. Leather Chem. Assoc. vol. 8 (1913) p. 62.
Z. angew Chem. vol. 26 (1913) p. 670.

Moeller, W.—TANNING WITH SULPHITE-CELLULOSE EXTRACT.

Sulphite-cellulose extracts contain lignosulphonic acids which are readily absorbed by hide substance and are very difficult to wash out. The sulphonic acids are the constituents which give the Procter-Hirst reaction (J. Soc. Chem. Ind. vol. 28 (1909) p. 293) and as they are so tenaciously retained, sulphite-cellulose extract cannot be detected in aqueous extracts of leather tanned with it (J. Soc. Chem. Ind. vol. 32 (1913) p. 373). Cold 2 per cent caustic-soda solution extracts these sulphonic acids from such leather, and on acidifying the solution gives the Procter-Hirst reaction. Sulphite-cellulose extract which has been used to "weight" fully-tanned leather is extracted by water alone. Hide tanned with a mixture of vegetable tanning material and sulphite-cellulose extract first absorbs the former, and if sufficient is present to tan the hide fully there is no absorption of the latter. (J. Soc. Chem. Ind. vol. 32 (1913 pp. 245,616.)

J. Soc. Chem. Ind. vol. 33 (1914) p. 365.
Collegium (1914) p. 152.
Ledertechn. Rundschau. vol. 2 (1910) p. 73.
Chem. Abs. vol. 8 (1914) p. 2082.

Moeller, W.—PSEUDO-TANNINS IN SULPHITE-CELLULOSE EXTRACTS.

Lime and sulphurous acid must be removed from the sulphite extracts before use. (Extracts from soda mills are only neutralized with a weak acid.) All cellulose extracts give about 15 per cent ash and contain rosin and sugar, which are without value and when mixed with real tannin extracts are concentrated in the tannin lye and have a detrimental effect. Molasses, cane sugar, and glucose are cheaper loading materials for leather than cellulose-liquor extracts. Only 50 per cent of the soluble cellulose extracts are utilized as loading material.

Collegium (1914) p. 319.
J. Soc. Chem. Ind. vol. 33 (1914) p. 654.
Pulp Paper Mag. Can. vol. 12 (1914) p. 468.
Paper vol. 14 (1914) No. 19 p. 18.

Moeller, W.—CELLULOSE EXTRACTS IN TANNING EXTRACTS.

The substances in cellulose extract which react with aniline and hydrochloric acid are all contained in the portion of it which is absorbed by hide. That the non-tannin filtrate sometimes gives the precipitate is due to the fact that many cellulose extracts are neutral or alkaline, and the material reacts very slowly with hide powder. Cellulose extract was detected in the suspender pits of a tannery in which its use had been discontinued for 6 months. By adding absolute alcohol to a fairly strong cellulose-extract solution 40-50 per cent is precipitated, which is quite a different action to that shown by most tanning materials. The precipitate contains all the substances which give the Procter-Hirst reaction (J. Soc. Chem. Ind. vol. 28 (1909) p. 293) and the portion left in solution is free from lignin. By precipitating the lignin substance there was obtained an oily liquid which was evaporated to a solid extract consisting mainly of substances absorbed by the hide. The alcoholic filtrate contained very little material capable of being absorbed by hide and did not react with aniline. Small quantities of cellulose extract mixed with other extracts can be detected by precipitating with alcohol and applying the Procter-Hirst test to the dissolved precipitate. The author found it impossible to detect cellulose extract in leather in the manufacture of which it has been used mixed with other extracts in the ordinary course of manufacture. When cellulose extract has been used as a filling and "weighting" material on tanned leather it can be washed out with water and the Procter-Hirst test applied.

Collegium (1914) p. 488.
J. Soc. Chem. Ind. vol. 33 (1914) p. 840.

Moeller, W.—WASTE SULPHITE LIQUOR AS TANNING MATERIAL AND ITS DETECTION IN LEATHER.

The tannin content of the extracts is found to be 24 per cent. The lignosulphonic acids contained in the extracts have a great affinity for the hide, but the tanning effect is low and the extracts are practically of no value for tanning purposes.

Z. angew. Chem. vol. 27 (1914) p. 560.
J. Am. Leather Chem. Assoc. vol 9 (1914) No. 5 p. 246.

DISCUSSION UPON THE SULPHITE-CELLULOSE EXTRACT AND ITS USE AS A TANNING MATERIAL.

Report on discussion in the Association of Leather Chemists.

Z. angew. Chem. vol. 27 (1914) p. 604.

Schulte, F. H.—SULPHITE LIQUOR AS TANNING MATERIAL AND ITS DETECTION IN LEATHER.

Polemic in answer to W. Moeller.

Ledertechn Rundschau vol. 6 (1914) p. 129.
Chem. Abs. vol. 8 (1914) p. 2637.
J. Am. Leather Chem. Assoc. vol. 9 (1914) No. 7 p. 335.

SULPHITE EXTRACT AND HOW TO DEAL WITH IT.

A discussion of its value and the opposition from the leather manufacturers. Deals particularly with W. Moeller's remarks of its uselessness. In Germany only 1·5 per cent of the output from all the sulphite-mills could be used in that country.

Papier-Fabr. vol. 12 (1914) Annual number p. 48.

Dickerson, W. H.—SULPHITE-CELLULOSE BLENDS.

Results of analyses of the mixture of sulphite-cellulose and various tanning extracts are given. A slight loss of tannin is shown, which was lessened by the use of small quantities (0·1-0·5 per cent) of acetic acid. Tests are recorded of liquors to which sulphite-cellulose has been added. Here no loss of tannin resulted but a decided gain occurred.

J. Am. Leather Chem. Assoc. vol. 9 (1914) p. 489.
J. Soc. Chem. Ind. vol. 33 (1914) p. 1163.

Gansser, A.—DETECTION OF SULPHITE-CELLULOSE EXTRACT.

Moeller and Loveland have been unable to confirm the author's results in the detection of cellulose extract in the extract from the leathers on which it has been used (Collegium (1912) p. 482). It must be assumed that there are some cellulose extracts which do not give the Procter-Hirst reaction (J. Soc. Chem. Ind. vol. 28 (1909) p. 293) and Becker has shown that such extracts may be produced. Quebracho wood which is kept away from light and air and under the action of mould growths will give the Procter-Hirst reaction.

Collegium (1914) p. 324.
J. Soc. Chem. Ind. vol. 33 (1914) p. 654.
Chem. Abs. vol. 9 (1915) p. 535.

Grothe, O.—TREATING WASTE SULPHITE LIQUOR.

The SO_2 is removed by adding lime, the liquor is concentrated and heated with cyanide of potassium or sodium, under pressure for 4-5 hours, to a temperature of 150°C. The reaction mass is diluted with water and an organic cyanogen compound is precipitated by the addition of an acid. The precipitate is filtered off and dried at ordinary temperature and may be used for tanning.

United States Patent 1087911 (1914)
Chem. Abs. vol. 8 (1914) p. 1357.
Paper Trade J. vol. 60 (1915) No. 6 p. 52.

Honig, M.—TANNING MATERIAL FROM WASTE SULPHITE LIQUOR.

The liquor is mixed with an acid, e.g. H_2SO_4, to form insoluble calcium salts and free a portion of the lignosulphonic acids, adding a soluble salt of the acid used (e.g. $ZnSO_4$) to convert the remaining calcium salts into other soluble salts and an insoluble calcium salt, and finally filtering the product through a material (e.g. oak galls or myrobalans) which forms insoluble compounds with iron.

United States Patent 1080970 (1913).
Chem. Abs. vol. 8 (1914) p. 591.

Appelius, W. and Schmidt, R.—DETECTION OF SULPHITE CELLULOSE IN TANNING EXTRACTS AND IN LEATHER.

The precipitate obtained with sulphite-cellulose extract and cinchonine sulphate forms, on heating, a characteristic, insoluble, brownish-black mass, which is quite distinctive even in solutions of vegetable tannins or in leather infusions containing only a little sulphite-cellulose extract. Neradol D. also gives with cinchonine sulphate a precipitate insoluble on warming, which, however, does not form a brownish-black mass but more resembles a silver-chloride precipitate.

The test depends upon the fact that the presence of tannin prevents the precipitate given by sulphite cellulose and cinchonine from being dissolved on heating. In case of pure sulphite extracts, tannin must be added before making the test.

Ledertechn. Rundschau vol. 6 (1914) p. 225.
Z. angew. Chem. vol. 27 (1914) p. 691.
Collegium (1914) p. 706.
J. Am. Leather Chem. Assoc. vol. 9 (1914) p. 64.
J. Soc. Chem. Ind. vol. 34 (1915) p. 189.

Paeszler, J.—ANALYSIS OF SULPHITE-CELLULOSE EXTRACTS.

Sulphite-cellulose extracts analysed by the official method of the International Association of Leather Trade Chemists gave results varying within 10 per cent according to the strength of the solution used for analysis, although such strengths were within the official limits of 0·35-0·45 per cent of tanning matter. In control experiments with vegetable tanning materials variations in the strength of the solution taken for analysis within these limits had no influence on the results. The German section of the Association has decided that the strength of the solution of sulphite cellulose for analysis should be 20 grammes of extract per litre.

Chem.-Ztg. vol. 38 (1914) p. 974.
J. Soc. Chem. Ind. vol. 34 (1915) p. 189.
Paper Trade J. vol. 61 (1915) No. 13 p. 50.

Becker, H. and Gross F. F.—SUSPECTED ADULTERATION OF QUEBRACHO EXTRACT WITH SULPHITE CELLULOSE.

An extract described as pure quebracho showed 15 per cent sulphite cellulose according to the Procter-Hirst reaction; a high alcohol figure, low gallic acid value, and high non-tannin content, also a large amount of sulphate in the ash.

Becker is of the opinion that quebracho extracts made from partly rotten wood might give such results. An extract from partly rotten wood indicated 20 per cent sulphite cellulose. Gross points out that only 2 per cent of rotten wood is allowed in commercial quebracho wood and that attempts to make from quebracho wood alone an extract showing figures like those of Becker's extract did not succeed. From experience he finds that quebracho extract cannot be regarded as pure if it contains more than 6 per cent of non-tannins.

Ledertechn. Rundschau vol. 6 (1914) Oct. 22.
Collegium (1915) p. 106.
J. Soc. Chem. Ind. vol. 34 (1915) p. 501.

Laufman, R.—DISTINCTION AND DETECTION OF TANNING MATERIALS AND CELLULOSE EXTRACT IN LEATHER.

In general it can be said that when leather is tanned partly with one extract and the tannage completed with another the aqueous infusion more nearly resembles the latter, but a part of the tannin in all cases may be so firmly combined with the hide fibre that it does not appear in the aqueous infusion. Leathers containing sulphite-cellulose extract, in which this material can be detected immediately after tannage, may show no reaction when tested after three months.

Ledertechn. Rundschau vol 6 (1914) Dec. 24 and 31.
J. Am. Leather Chem. Assoc. vol. 10 (1915) p. 160.
J. Soc. Chem. Ind. vol. 34 (1915) p. 437.

Harrocks, W. E. and Tullis, J. K.—PRODUCTION OF TANNING EXTRACTS FROM WASTE WOOD-PULP EXTRACTS.

Wood-pulp extracts obtained as waste products in the manufacture of paper pulp, etc., are heated with neutral soluble salts, (e.g. aluminium sulphate and magnesium sulphate) and the mass which separates is pressed, dissolved in warm water, and used for tanning.

English Patent 18332 (1914).
J. Soc. Chem. Ind. vol. 34 (1915) p. 1063.

TANNIN EXTRACT FROM WASTE SULPHITE LIQUOR.

Embretsfos mills are now producing 400,000 kilogrammes (880,000 lb.) extract yearly by Landmark's method but the production can be increased to 5,000-6,000 metric tons a year (5,500-6,600 short tons). Price at present is 20 ore per kilogramme ($0.0245 per lb.). The Norwegian barium extract makes the leather firmer and more pliable and gives a lighter colour, and there is a great demand for the extract in Norway as well as in other countries.

Papier-Fabr. vol. 3 (1915) No. 15 p. 188.

Luke, J.—PROCESS FOR OBTAINING A COLOURLESS, TECHNICAL, LIME-FREE TANNIN EXTRACT FROM WASTE SULPHITE LIQUOR.

Sodium or potassium bicarbonate alone or in mixture with phosphoric acid or with ammonia and phosphoric acid is used for precipitation of the lime.

Norwegian Patent 26138 (1915).
Papier-Fabr. vol. 3 (1915) No. 17 p. 215.

Grothe, O.—PROCESS OF MANUFACTURING A TANNING MATERIAL FROM WASTE SULPHITE LIQUOR.

Norwegian Patent 25315 (1915).
Papir. J. vol. 3 (1915) p. 37.

Hurt, H. H.—TANNING MATERIAL FROM WASTE SULPHITE LIQUOR AND PROCESS OF PREPARING THE SAME.

A neutral highly concentrated waste sulphite liquor is treated successively or simultaneously with sulphuric acid and alkali sulphate to remove lime and to liberate ligninsulphonic acids. The precipitate is separated leaving a tanning liquor of 28° to 31°Bé. (Specific gravity 1·24-1·27.)

United States Patent 1147245 (1915).
J. Soc. Chem. Ind. vol. 34 (1915) p. 915.
Chem. Abs. vol. 9 (1915) p. 2465

Landmark, H. B.—PREPARATION OF A TANNING EXTRACT FROM WASTE SULPHITE LIQUOR.

Waste liquors are evaporated to less than half their original bulk to remove free SO_2, then treated with sodium carbonate in about twice the quantity necessary for neutralization to remove the iron and part of the calcium, and, after filtering or decanting the liquor, the remainder of the calcium is precipitated by oxalic acid. A further quantity of organic acid is added to the filtered product which is then concentrated.

French Patent 474336 (1914).
J. Soc. Chem. Ind. vol. 34 (1915) p. 1005.

Landmark, H. B.—TANNING EXTRACT FROM WASTE SULPHITE LIQUOR.

Sulphuric acid may be used instead of oxalic acid.

English Patent 7090 (1915).
See French Patent 474336 (1914).
J. Soc. Chem. Ind. vol. 35 (1916) p. 372.
Chem. Abs. vol. 10 (1916) p. 2813

Appelius, W.—CINCHONINE FOR THE DETECTION OF SULPHITE CELLULOSE IN LEATHER.

The cinchonine test is uncertain with leather extracts unless carried out according to the following method:—Five to ten grammes of leather, cut into small cubes (not finely ground), is extracted by heating to boiling with 100 c.c. of water. After filtration, 5 c.c. of 25 per cent hydrochloric acid is added to the filtrate which is heated to boiling and again filtered. Twenty c.c. of cinchonine solution is then added to 50 c.c. of the filtrate, together with a very little tannin solution, and the mixture heated to boiling without moving the flask. A lumpy, brown-black precipitate appears in the presence of even small amounts of sulphite cellulose.

J. Am. Leather Chem. Assoc. vol. 10 (1915) p. 202.
Ledertechn. Rundschau vol. 7 (1915) p. 17.
J. Soc. Chem. Ind. vol. 34 (1915) p. 501.

Gross, F. F.—METHOD OF PRODUCING TANNING COMPOSITIONS FROM WASTE SULPHITE LIQUOR.

The warm liquor after treatment with hydrochloric and sulphuric acids and potassium chromate, to remove lime, is concentrated to about 20° Bé. (specific gravity 1.16), filtered, and further concentrated as desired.

United States Patent 1154762 (1915).
J. Soc. Chem. Ind. vol. 34 (1915) pp. 1155, 1139
Chem. Abs. vol. 9 (1915) p. 3378.

Byrom, F. G.—PROCESS OF MANUFACTURING TANNING EXTRACTS FROM SULPHITE-CELLULOSE LIQUOR.

Concentrated sulphite liquors are treated with phenols, amino compounds or napthalene-disulphonic acid, or with mixtures of these, or with the middle oil or the heavy oil from the distillation of coal-tar. A soluble, light-coloured tanning agent is obtained.

English Patent 24196 (1914).
J. Soc. Chem. Ind. vol. 34 (1915) p. 1063.
Chem. Abs. vol. 10 (1916) p. 1610

Landmark, H. B.—WASTE SULPHITE LIQUOR AS A TANNING MATERIAL.

The author discusses the problem in general and states that the "sulphite extracts" when used in mixture with other extracts improve the colour of the leather, cause a greater absorption, and accordingly reduce the cost of tannage. The extracts are not good unless the iron is absolutely removed and the lime removed to such an extent that it cannot be detected in the extract (only in the ash). Tables showing the composition of various extracts.

Tid. Kemi. Farm. Terapi. vol. 9 (1916) Nos. 1 and 2.

Beveridge, J.—THE UTILIZATION OF WASTE SULPHITE LIQUOR.

When the liquor is neutralized with lime and the clear liquor evaporated down, it can be sold as a tanning agent known on the market as "spruce liquor". The table gives a comparison of this commodity with the extract from hemlock bark.

——	Spruce Sulphite Process.	Hemlock Wood Sulphite Process.	Hemlock Bark Extracted with Water only.
	%	%	%
Moisture	41.34	47.93	54.24
Total solids	58.68	52.07	45.76
Soluble solids	58.61	51.93	41.93
Insoluble	.07	.14	3.83
Non-tannins	39.36	24.84	16.63
Tannins	19.25	27.09	25.30
Specific Gravity	1.290	1.269	1.215

If calculated on 100 parts of total solids the amount of tannin is respectively 32·80 per cent, 52·02 per cent, and 55·29 per cent. The fact that this tannin is associated with other organic compounds in combination with lime and sulphurous acid and that these have the tendency to foul the tan liquor in the pits and perhaps enter into the composition of the leather itself, has operated against its extended use. Processes for a separation of these substances have been proposed by Mitscherlich, Opl, Kempe, Kumpfmiller and others.

J. Soc. Chem. Ind. vol. 35 (1916) p. 563.

Laufman, R.—DETECTION AND DIFFERENTIATION OF VEGETABLE AND SYNTHETIC TANNINS.

Reactions for detection of sulphite-cellulose extract and artificial tannins of the Neradol class. Finely-divided leather is allowed to stand overnight in ten times its weight of 2 per cent caustic soda solution. The solution is then filtered, slightly acidified with hydrochloric acid, filtered again, and diluted so as to contain 0·6 per cent of organic matter. It is then tested by the aniline test or by cinchonine sulphate. A negative result shows absence of both sulphite cellulose and Neradol. A positive result indicates sulphite cellulose if Neradol is subsequently proved to be absent by special tests. Tests on Neradol are given.

Chem.-Ztg. vol. 41 (1917) pp. 273 and 286.
J. Soc. Chem. Ind. vol. 36 (1917) p. 513.

Harvey, A.—SULPHITE-CELLULOSE EXTRACTS.

Review of method of manufacture, uses and tests.

Leather World vol. 9 (1917) p. 73.

ALCOHOL

The amount of fermentable sugar in the waste sulphite liquor ordinarily varies according to the published data, between 1·5 and 2 per cent, but may in some cases be as high as 2·4 per cent. (Canadian sulphite liquor will vary from 0·5 to 1·75 per cent of fermentable sugars). As the lower carbohydrates of the wood must be considered as the chief source of the fermentable sugar, the amount of sugar in the liquor may vary to some extent with the wood material, but no doubt the greatest factor in these variations is to be found in the method of cooking. Hagglund, who has published a very instructive work on the present stage of alcohol production from waste sulphite liquor, calls attention to this fact and shows how the formation of sugar depends upon the strength of the liquor as well as upon the temperature. He also shows how the fermentable sugars are partially destroyed at the high temperature prevailing in the digester at the end of the "cook". It is also interesting to note that only very little sugar is formed from the cellulose in the cooking process. The idea of manufacturing alcohol from the waste liquor dates back to the early years of the sulphite pulp industry but not until recent years had this resulted in commercial processes of any importance. Wallin's and Ekstrom's processes are now in operation on a commercial scale in Sweden and the United States and, presumably, to a great extent in Germany; in Norway, Landmark's process has been in operation for some time, and a plant is also established in Sweden for the operation of the same process. Marchand's process has been tried out in an experimental plant in the United States with satisfactory results. The principle is the same in all these processes. The free sulphurous acid must be removed as far as possible from the liquor and recovered, which in some cases is partly effected by concentration of the liquor. The liquor is then neutralized to a certain point of acidity. A suitable yeast is then added and the liquor fermented and distilled. The yield of alcohol depends of course, in the first place, upon the amount of fermentable sugar in the liquor, but the neutralization as well as the fermentation are both processes which require the closest control if the highest possible yield is to be obtained. Although a yield as high as 1·4 per cent by volume has in some cases been obtained Hagglund gives 1·0 per cent (100 per cent alcohol) as a good average. Landmark claims a higher yield, namely 1·2 per cent, with his process and an average of 1·1 per cent, and Marchand's process is said to yield 1—1·25 per cent, 180 proof alcohol.

With regard to the neutralization of the liquor (which usually is previously or simultaneously effectively aerated in order to oxidize certain reducing organic substances) it is not advisable to use lime alone, as in this case a large excess is required, causing an appreciable amount of sugar to be destroyed. Another objection is that it is difficult to obtain a clear solution which is necessary for the fermentation. According to Hagglund, by using a smaller quantity of lime and employing calcium carbonate for the final neutralization these troubles are eliminated. In the Marchand process barium carbonate is employed for neutralization whereas Landmark uses calcium carbonate in his process.

Nitrogen and phosphates are not present in the liquor in the quantity required for a normal fermentation, and must be added to the neutralized liquor. Certain available yeast extracts contain the necessary amount of these substances but if other extracts are used the nutriment must be added in a suitable form. In Landmark's process milk or whey is heated with acid, the precipitate of "lignocasein" is filtered off, and the filtrate added to the sulphite liquor which can then be fermented directly with ordinary brewers' yeast. Ekstrom's process requires a "tempered" yeast which is prepared to meet the special conditions of the sulphite liquor. With regard to the details of the processes of fermentation and distillation reference may be made to Hagglund's publication "Die Sulfitablauge und ihre Verarbeitung auf Alkohol". In this same publication the manufacturing cost of a 100 per cent spirit is calculated, assuming a recovery of 3.7 cub. m. (816 gallons) of liquor per metric ton (2204 lb.) of air-dry pulp [4.1 cub. m. (904 gallons) per metric ton (2204 lb.) of bone-dry pulp] as follows:—

MANUFACTURING cost for 1 cubic metre (220 gallons) of distilled mash.

Cost Items.	SIZE OF MILL.					
	33,075 short tons.		22,050 short tons.		11,025 short tons.	
	Marks.	$	Marks.	$	Marks.	$
Steam	0·422	0·1000	0·422	0·1000	0·422	0·1000
Nutriment	0·083	0·0197	0·083	0·0197	0·083	0·0197
Neutralization	0·167	0·0397	0·167	0.0397	0·167	0·0397
Materials	0·022	0·0052	0·028	0·0066	0·040	0·0095
Repairs	0·055	0·0131	0·078	0·0186	0·117	0·0279
Labour	0·165	0·0393	0·225	0·0535	0·335	0·0796
Salaries	0·070	0·0168	0·090	0·0214	0·123	0·0292
Miscellaneous	0·056	0·0133	0·067	0·0159	0·073	0·0174
	1·040	0·247	1·060	0·276	1·360	0·324

These figures are based upon prices in Scandinavia, and would have to be changed to suit American conditions. Assuming a 50 per cent increase in salaries, labour, and repair costs the manufacturing cost would be $0.282, $0.323, and $0.392. The yield of 100 per cent spirit being on an average 1 per cent by volume, and calculating the cost of an alcohol plant in America as being 50 per cent higher than in Scandinavia, and further allowing for 15 per cent depreciation and interest the total cost and selling price of one litre 100 per cent spirit is given in the following table.

Size of Pulp-mill Short Tons.	Cost of alcohol Plant.	15 per cent Amortization and interest of plant.	Spirit Produced.	Amortization and interest per litre spirit.	Manufacturing cost.	Selling price.
	$	$	Litres.	$	$	$
33,075	150,000	22,500	1,110,000	0·0202	0·0282	0·0484
22,050	112,500	16,900	740,000	0·0229	0·0323	0·0552
11,025	75,000	11,250	370,000	0·0315	0·0392	0·0707

The corresponding prices of an imperial gallon are $0.220, $0.251, and $0.320 and of a United States gallon $0.183, $0.209, and $0.268.

Landmark claims a higher yield of alcohol, namely an average 1·1 per cent, and a lower cost of production, namely $0.0254 per litre, depreciation and interest and cost of handling included. This corresponds to a price of $0.115 per imperial gallon or $0.096 per United States gallon manufactured in Scandinavia. A direct comparison of the two processes on the basis of the published figures is not possible, as the operating cost varies considerably with the size of the plant and with the yield of alcohol. Landmark has based his calculations on a recovery of 6·5 cub. m. (1,430 gallons) liquor per metric ton (2,204 lb.) of pulp and upon plant connected with a 15,000 metric tons (17,000 short tons) pulp-mill. This would mean a yearly production of 1,072,500 litres (236,000 gallons) of alcohol and would require an alcohol plant of the same size as the 30,000 metric ton (33,075 short tons) pulp-mill in the previous example. The chief difference of the two processes is in the neutralization and fermentation, but even if the cost of nutriment, neutralization, and material is subtracted the manufacturing price would still be as high as $0.186 for an imperial gallon or $0.158 for a United States gallon of 100 per cent spirit, which is appreciably higher than the cost calculated by Landmark. The value of the "lignocasein" recovered in this process is said to cover very nearly the cost of the milk or whey employed.

As the fermentable sugars represent only 15-20 per cent of the total organic substances in the liquor, the residual liquor from the distillation process should be further utilized. Fuel may be recovered according to Strehlenert's process, but it has been pointed out that an unfavourable precipitate is obtained in cases where much lime has been used for neutralization. Valuable products may also be obtained by destructive distillation of the dry substance.

In the cooking process 7 kilogrammes (14 lb.) methyl alcohol are formed per ton (short) of pulp of which 4·4 lb. can be recovered from the relief gases. One part of this alcohol is lost during the various operations, so that the crude ethyl alcohol contains about 3·2 per cent methyl alcohol. The two alcohols can be separated but of course this is not necessary when the spirit is to be used for industrial purposes.

Mitscherlich, A.—INNOVATIONS IN THE PROCESS OF PRODUCING TANNING MATERIALS WITH THE PRODUCTION OF THE BY-PRODUCTS CELLULOSE, GUMS, ACETIC ACID, AND CALCIUM BISULPHITE.

German Patent 4179 (1878).
(See "Tanning Materials" p. 78.)

Mitscherlich, A.—COOKING OF WOOD WITH CALCIUM BISULPHITE, RECOVERING CELLULOSE TANNING MATERIALS, GUMS, AND ACETIC ACID.

English Patent 1668 (1882).
(See "Tanning Materials" p. 78.)

Pictet and Brelaz.—IMPROVEMENTS IN SULPHITE WOOD-PULP.

Recovery of gum, rosin, tannin, and alcohol.

English Patent 9509 (1884).
(See "Tanning Materials" p. 78.)

Mitscherlich, A.—PROCESS FOR PRODUCING TANNING MATERIALS, ADHESIVES, AND OTHER SUBSTANCES FROM WASTE SULPHITE LIQUOR.

German Patent 72161 (1891).
English Patent 12927 (1893).
(See "Tanning Materials" p. 78.)

Mitscherlich, A.—PROCESS FOR PREPARATION OF ADHESIVES FROM HORN SUBSTANCES BY MEANS OF WASTE SULPHITE LIQUOR.

The waste liquor can be used for the production of alcohol after the tannins have been removed.

German Patent 82498 (1893).
(See "Gums, Adhesives, and Sizing Materials" p. 68.)

Mitscherlich, A.—PROCESS AND APPARATUS FOR UTILIZATION OF WASTE SULPHITE LIQUOR.

Covers German patents for reclaiming adhesives, tanning material, alcohol, and fodderstuff.

Austrian Privilegium 112 (1894).
(See "Gums, Adhesives, and Sizing Materials" p. 68.)

Classen, A.—PROCESS FOR MAKING SUGAR SOLUTIONS FROM TANNIN-CONTAINING WOODS OR OTHER CELLULOSE MATERIALS EASILY FERMENTABLE.

The product obtained by the usual method of inversion from the tannin-containing woods can be fermented to only a slight extent due to the gallic acid produced from the tannins. To get rid of this gallic acid it is precipitated in the form of a metallic salt by first neutralizing with $CaCO_3$ and then adding a solution of a metallic salt (e.g. $FeSO_4$). It is then made weakly alkaline with lime, and the precipitated $CaSO_4$ filtered off.

German Patent 161644 (1903).
Chem. Zentr. (1905) part II p. 560.

Ekstrom, G.—SPIRIT FROM WASTE SULPHITE LIQUOR.

Svensk Kem. Tid. (1909) No. 7.
Papier-Ztg. vol. 35 (1910) part II p. 2519.

Tillberg, E. W.—PROCESS FOR OBTAINING TANNINS, ALCOHOL, AND CELLULOSE FROM WOOD.

Swedish Patent 25283 (1907).

Bergstrom, H. O. V.—METHYL ALCOHOL IN THE MANUFACTURE OF ETHYL ALCOHOL FROM WASTE SULPHITE LIQUOR.

Jernkontorets Annaler (1909) p. 691.
Papier-Fabr. vol. 7 (1909) pp. 506, 607.

Bergstrom, H. O. V.—METHYL ALCOHOL IN DIGESTION OF SULPHITE WOOD-PULP.

Methyl alcohol has been obtained in considerable quantities from the condensed vapours blown off after the digestion of wood by the soda process. The author has examined the similar distillate from the sulphite-pulp digesters and has found that it contained about 1 per cent methyl alcohol. Only a portion of the total methyl alcohol formed passes off with the vapours, a certain amount remaining behind in the waste liquors. This latter observation has a bearing on the proposed utilization of these waste liquors for the production of ethyl alcohol by fermentation. In connection with the question of the chemical constitution of wood, the author mentions that when wood is boiled under atmospheric pressure with a dilute solution of an alkali hydroxide, ammonia, methyl alcohol, acetaldehyde, and acetone are formed. The same products are also formed from peat and "white moss" but in different proportions.

Papier-Fabr. vol. 8 (1909) p. 970.
J. Soc. Chem. Ind. vol. 28 (1909) p. 1162.

Rosenblatt and Rosenband, M.—THE RETARDING ACTION OF CERTAIN ACIDS UPON ALCOHOLIC FERMENTATION.

Chem.-Ztg. vol. 33 (1909) p. 921.

MANUFACTURE OF ALCOHOL FROM WASTE SULPHITE LIQUOR ACCORDING TO EKSTROM'S PATENT, IN SKUTSKAR (SWEDEN).

Papier-Ztg. vol. 34 (1909) part I p. 1682.

Wallin, J. H.—ALCOHOL FROM WASTE SULPHITE LIQUOR.

Neutralization with lime in excess and subsequent saturation with carbon dioxide. Addition of yeast and malt to the filtrate. In order to increase the sugar content the waste liquor may be cooked at high temperature with peat or sawdust.

Norwegian Patent 18687 (1908).
Swedish Patent 267808 (1907).
German Patent 246708 (1908).
Chem.-Ztg. vol. 33 (1909) Rep. p. 251.
Papier-Ztg. vol. 35 (1910) No. 16.
Chem. Zentr. (1912) part I p. 1871.
Pulp Paper Mag. Can. vol. 10 (1912) p. 358.

Stora Kopparbergs Bergslags Aktiebolag.—PROCESS FOR OBTAINING ALCOHOL FROM THE WASTE LIQUORS OF THE MANUFACTURE OF WOOD-PULP BY SOLUBLE SULPHITE.

The lime sludge from sulphate-pulp mills which, besides calcium carbonate, contains organic matter and salts of sodium and magnesium, obtained as a waste product in the treatment of the waste liquors with sodium sulphate or carbonate, is used to neutralize the waste liquor, which contains in addition to glucose and other organic substances a small quantity of calcium bisulphite and free sulphurous acid. Not only is neutralization thus effected but the liquor is also enriched with nutritive substance necessary for the subsequent fermentation. If necessary the liquor is rendered neutral or slightly acid by addition of acid or alkali, and is then separated from the precipitate. The liquor is then cooled, preferably by being sprayed down from the top of a tower and encountering a current of air moving upwards; by this treatment, it is also concentrated and saturated with air. It is then treated with an enzyme preparation or with yeast, and with nutriment yeast extract, the alcohol formed being separated by distillation or otherwise.

French Patent 402331 (1909).
J. Soc. Chem. Ind. vol. 28 (1909) p. 1221.
Wochbl. Papierfabr. vol. 40 (1909) p. 4265.
Papier-Ztg. vol. 43 (1909) p. 1682.

Ekstrom, G.—ALCOHOL FROM SULPHITE-CELLULOSE LYES.

An experimental plant for the production of alcohol from sulphite-cellulose waste lyes at Skutskar, Sweden, began operations on May 24, 1909, the waste lyes from a cellulose works of 5,000 metric tons (5,500 short tons) capacity being treated. In March 1910, 2,130 litres (469 gallons) of spirit of "normal strength" were produced per 24 hours, total for the month was 49,027 litres (10,800 gallons). In April the production was 2,120 litres (467 gallons) per 24 hours, total 50,980 litres, (11,200 gallons). In consequence of the favourable results the plant is now being extended to deal with the waste lyes from the whole production of the Skutskar cellulose works 20,000 metric tons (22,000 short tons) per annum.

Papier-Fabr. vol. 8 (1910) p. 582.
J. Soc. Chem. Ind. vol. 29 (1910) p. 810.

Wallin, J. H.—SULPHITE SPIRIT.

Wallin produces up to 1.5 per cent alcohol by volume from waste liquor in the Boksholm sulphite mill. The experimental plant in Kopmanholmen obtained from waste liquor from one metric ton (2204 lb.) of pulp 50 litres (11 gallons) of spirit.

Papier-Ztg. vol. 35 (1910) pp. 1588, 2519.
Wochbl. Papierfabr. vol. 40 (1909) p. 4253.

Schwalbe, C. G.—ALCOHOL FROM SULPHITE LYE.

In 1891 Lindsey and Tollens made an investigation of a sulphite-cellulose waste lye, containing 9-10 per cent of dry solids, and found in it 1.2 per cent of fermentable sugars, the yield in alcohol being 58-67 litres (12.8-14.7 gallons) per metric ton (2204 lb.) of cellulose. Recently in Sweden, Wallin at Forss, and Ekstrom at Skutskar (see J. Soc. Chem. Ind. (1910) p. 810) have attempted to develop an industrial process on this basis. The two processes are identical in all essentials except for the neutralization of the crude-acid lyes; the former uses lime and the latter the waste causticization sludge from the sulphate cellulose mills. The lyes are first neutralized in large vats; they are then cooled, (e.g. in towers), and are simultaneously aerated. It is claimed that the neutralization sludge obtained in the filter presses after this, process if used for the preparation of fresh lyes, contains sufficient calcium sulphite to effect a saving of 40-45 per cent of the sulphur required. In a mill producing 10 metric tons (11 short tons) of cellulose per 24 hours the volume of the lyes to be treated amounts to about 100 cub. m. (22,000 gallons) per day and the quantity of neutralization sludge may be taken at about 1.5 metric tons (1.7 short tons) dry or 3 metric tons (3.3 short tons) moist. A yeast nutriment, malt extract or dead yeast is added to the neutralized, cooked, and aerated liquid, which is transferred to the fermentation tuns. These must be large enough to allow a storage of at least 3 days' duration. After fermentation and separation of the yeast, the lye is distilled in a continuous still. The column apparatus designed by Kubierschky is particularly suitable for the distillation of sulphite lyes. The alcohol in these is in an extremely dilute condition and the consumption of steam in their distillation is far larger than in a molasses distillery. The alcohol obtained is already denatured; it contains considerable proportions of methyl alcohol pre-existing in the unfermented lyes, furfural, and probably acetone; it appears to be practically free from terpenes. The process is being worked on a considerable scale at Skutskar; the average yield of alcohol may be taken as 60 litres (13.2 gallons) per metric ton (2,204 lb.) of cellulose and the present output is 50,980 litres (11,200 gallons) monthly. It is stated that under Swedish conditions the treatment shows a profit, but the author points out that it offers no solution of the problem of the disposal of the waste lyes; on the contrary it may even happen that owing to the presence of dead yeast, etc., in the spent wash the nuisance may be aggravated rather than abated.

Wochbl. Papierfabr. vol. 41 (1910) p. 2354.
Z. angew. Chem. vol. 23 (1910) pp. 1080, 1537.
J. Soc. Chem. Ind. vol. 29 (1910) p. 1052.
Papier-Ztg. vol. 35 (1910) p. 2004.
Chem. Abs. vol. 5 (1911) p. 196.

Kiby, W.—ALCOHOL FROM SULPHITE LIQUOR.

The author discusses the economic aspects of the newly established industry of the manufacture of spirit from the waste lyes of sulphite wood-pulp mills, taking as a basis the average yield of 60 litres (13·2 gallons) of absolute alcohol per metric ton (2,204 lb.) of cellulose produced. The prospects of the industry depend on the cost of production, the capacity of the market, and the condition of taxation. In Sweden all the conditions are more favourable than in Germany. The total production of absolute alcohol in Sweden for the financial year 1908-9 was about 32 million litres (7,040,000 gallons) whilst imports amounted to 1·17 million litres (257,000 gallons). The sulphite-pulp mill at Larkudden is now producing spirit at the rate of 600,000 litres (132,000 gallons) per annum and will soon be in a position to produce 1·2 million litres (264,000 gallons), so that the whole of the imports would be equalled by the product of this single mill. The pulp-mills of Sweden are capable of producing about 25 million litres (5,500,000 gallons) of absolute alcohol, and since the manufacture of spirit from the ordinary raw materials is intimately bound up with the other branches of agricultural industries it is hardly conceivable that the new sulphite spirit will be allowed to displace any considerable proportion of the present production. Further, since the sulphite spirit is of the denatured spirit, owing to its impurities, it must be conceded that the future of the industry depends on the opening up of new industrial sources of consumption. The author details the probable cost of production of spirit at a mill producing 60 metric tons (66 short tons) of cellulose per day. Such a mill could produce 1·3 million litres (286,000 gallons) of absolute alcohol per annum at a cost of 10 pfennigs ($0.024) per litre ($0.109 per gallon) allowing 10 per cent for depreciation of capital. In Sweden the larger distilleries bear a heavier tax the larger their production, so that including this tax 1·3 million litres (286,000 gallons) per annum could be produced for about 17 shillings ($4.14) per 100 litres ($0.188 per gal.) With the increasing consumption of industrial alcohol it is possible that even the full production of Swedish sulphite spirit could gradually be absorbed. Turning to Germany the author estimates that the maximum annual production of sulphite spirit might be about 33 million litres (7,260,000 gallons), which would be added to the present total production. The excise regulations in Germany are particularly severe and expressly penalize new distilleries, so that in addition to the production cost of 10-11 shillings ($2.44, $2.68) per 100 litres ($0.11, $0.122 per gal.) the sulphite spirit would be subject to an excise charge of 19 shillings ($4.63) per 100 litres ($0.21 per gal.). German wood-pulp manufacturers could therefore only produce the spirit at a loss, which they would not consent to bear unless the production of spirit would offer a solution of the problem of the ultimate disposal of the waste lyes. This, however, is hardly likely to be the case, since the spent wash would in all probability be just as obnoxious as the original lye.

Chem.-Ztg. vol. 34 (1910) pp. 1077, 1091.
J. Soc. Chem. Ind. vol. 29 (1910) 1265.
Chem. Abs. vol. 5 (1911) p. 785

Ekstrom, G.—ALCOHOL FROM SULPHITE LIQUORS.

Alcohol is produced from the waste lyes obtained from the digestion of wood, etc., by the bisulphite process, by first precipitating the excess of sulphites and sulphurous acid by means of lime, chalk or other suitable neutralizing agent, concentrating the liquor, cooling to a temperature of 25°C., and fermenting the saccharine constituents by the addition of yeast and a yeast nutriment. The yeast nutriment is prepared from brewers' yeast or from yeast collected from an earlier fermentation by heating the yeast for a comparatively long time at a temperature of about 45°C., at which temperature the yeast is digested by the action of an enzyme contained in it.

English Patent 6741 (1910).
Canadian Patent 132717 (1911).
J. Soc. Chem. Ind. vol. 30 (1911) p. 504.

Matheus.—ALCOHOL FROM SULPHITE LIQUOR.

The author made experiments in 1892 on fermentation of sulphite liquor. Yield 0.7 per cent by volume.

Papier-Fabr. vol. 8 (1910) p. 532.
Z. angew. Chem. vol. 23 (1910) p. 1584.

Bergstrom, H.—METHYL ALCOHOL FROM THE MANUFACTURE OF CELLULOSE.

Methyl alcohol is formed in the sulphite as well as in the sulphate digestion. One metric ton (2,204 lb.) of cellulose produced in the sulphate cooking is accompanied by 13 kilogrammes (28.6 lb.) of methyl alcohol, while in the sulphite process 10 kilogrammes (22 lb.) are produced. It is not practicable to separate the methyl alcohol from the ethyl alcohol produced by the fermentation of sulphite liquor.

Papier-Fabr. vol. 8 (1910) p. 506.
Z. angew. Chem. vol. 23 (1910) p. 1823.

ETHYL ALCOHOL FROM SULPHITE LIQUOR.

Discussion on Schwalbe's paper. The employment of sulphite liquor for fermentation may be impossible in Germany on account of the heavy taxes. The sugar solution obtained from wood by hydrolysis could be used directly as a cattle food.

Papier-Ztg. vol. 35 (1910) p. 2044.
Z. angew Chem. vol. 23 (1910) p. 2057.

WOOD SPIRIT FROM WOOD, ETC.

For one metric ton (2,204 lb.) of sulphite pulp 10 kilogrammes (22 lb.) of wood spirit (methyl alcohol, acetone, and aldehyde) are formed.

Jernkontorets Annaler (1909) No. 11.
Papier-Fabr. vol. 7 (1909) p. 1314.

Segerfeld, B.—ALCOHOL FROM WASTE SULPHITE LIQUOR.

History. Formation of fermentable sugars from wood and wood-gum. Quantity and composition of waste liquor. Neutralization and concentration. Precipitation of lime and recovery of same.

"Kemi och Bergwetenskap" (Techn. Tid.)
Papier-Ztg. vol. 35 (1910) pp. 2518, 2558.

SPIRIT FROM WASTE SULPHITE LIQUOR.

The Company "Ethyl" in Falum (Sweden) will operate Wallin's patent for the manufacture of sulphite spirit.

Papier-Ztg. vol. 35 (1910) p. 2118.
Papier-Fabr. vol. 8 (1910) p. 311.

ALCOHOL FROM WASTE SULPHITE LIQUOR.

Reports on the manufacture in Sweden. No reduction in volume of effluent to be expected. Opinions differ with regard to the injurious effect of the effluent.

Svensk. Pap. Tid. (1910).
Papier-Ztg. vol. 35 (1910) pp. 569, 649, 690, 1110, 1387.

Ekstrom, G.—MANUFACTURE OF SPIRIT FROM WASTE SULPHITE LIQUOR.

Paper read before the Swedish Technical Association. The waste liquor is mixed with lime sludge from the sulphate-pulp process and fermented in large vats.

At the present time 30 million litres (6,600,000 gallons) sulphite spirit could be produced in Sweden and 250 million litres (55 million gallons) in the whole world. The price is 46-57 ore ($0·13) per litre ($0·585 per gallon). At 20 ore ($0·054 per litre ($0·245 per gallon) it could be used for motors.

Svensk. Kem. Tid. (1907) No. 7.
Chem.-Ztg. vol. 34 (1910) p. 223.
Wochbl. Papierfabr. vol. 41 (1910) p. 638.
Papier-Fabr. vol. 8 (1910) pp. 238, 582.
Papier-Ztg. vol. 35 (1910) pp. 649, 690.
J. Soc. Chem. Ind. vol. 29 (1910) p. 810.

Smart, B.—SULPHITE SPIRIT.

An acid is added to the waste liquor with simultaneous oxidation with air. Afterwards the liquor is neutralized and fermented.

Swedish Patent 31956 (1909).
Chem. Abs. vol. 6 (1912) p. 2316.

Ekstrom, G.—UTILIZATION OF REMAINING SUBSTANCES AFTER DISTILLATION.

In order to recover the organic matters an organic or inorganic base or a mixture of both is added to the distillation residue, which may be oxidized or reduced eventually using a contact substance previous to the treatment with basic substances.

Swedish Patent 32127 (1910).
Canadian Patent 137007 (1911).
Chem. Abs. vol. 6 (1912) p. 2316.
Paper vol. 10 (1912) No. 9 p. 16.

Foth, G.—MANUFACTURE OF SPIRIT FROM WOOD WASTE AND WASTE SULPHITE LIQUORS.

Estimation of manufacturing cost. Under the present rate of taxation the manufacture is not feasible in Germany. It cannot be used for drinking purposes, as it contains large quantities of methyl alcohol and other by-products.

Z. Spiritusind. (1910) p. 589.
Chem.-Ztg. vol. 35 (1911) Rep. p. 35.
Chem. Abs. vol. 5 (1911) p. 1970.

Norton, T. H.—ALCOHOL FROM SULPHITE LIQUOR.

For every ton of cellulose made by the sulphite process there are 10 tons of waste lyes. Among the matters present are dextrose and various other sugars, xylose, acetic acid, tannic acid, nitrogen compounds, resins, etc., as well as the calcium ligninsulphonate, the chief product of the reaction. Of the sugars present most are susceptible of fermentation. They constitute about 1 per cent of the lyes. The liquid is first neutralized with calcium carbonate, after which yeast is introduced. When the fermentation is complete the alcohol produced is secured in the ordinary manner. The process yields 6 gallons of alcohol (100 per cent) for 1,000 gallons of lye. About 14 gallons are secured to every ton of cellulose. Methyl alcohol and other volatile compounds are contained in this crude alcohol. It is used as denatured alcohol for heating and technical purposes. The excise rates in Sweden have been adjusted so as to aid this new industry. If the process were extended to all Swedish sulphite works the annual output would be about 3,500,000 gallons. It is doubtful whether a sufficient demand exists for this grade of alcohol to furnish a home market for such an amount. German chemists are sceptical as to the possibility of producing the alcohol economically under existing conditions in the Empire, where, on a basis of the Swedish results, over 800,000 gallons could be produced annually.

United States Consular Report.
J. Soc. Chem. Ind. (1911) p. 1466.
World's Paper Trade Rev. vol. 56 p. 1236.
Chem. Abs. vol. 6 (1912) p. 929.

Lassar-Cohn—SPIRIT FROM WASTE SULPHITE LIQUOR.

The alcohol legislation prevents the introduction of the manufacture of alcohol in Germany.

Papier-Ztg. vol. 36 (1911) p. 677.

Voerkelius.—MANUFACTURE OF SPIRIT FROM CELLULOSE MATERIALS.

Sulphite spirit for light and power can not be manufactured in German mills, as this spirit is subjected to taxation and would be about twice as expensive as benzine.

Wochbl. Papierfabr. vol. 42 (1911) p. 853.

COST OF MANUFACTURE OF SULPHITE SPIRIT.

Experience in the plant at Kopmanholmen in Sweden shows the cost of 1 litre of 100 per cent spirit at a 12,000 metric ton (13,200 short tons) sulphite-mill to be 9.5-10.6 ore ($0.025-$0.029, equivalent to $0.114-$0.132 per gallon). By recovery of lime and sulphur this is reduced by 6-7 ore ($0.016-$0.019, equivalent to $0.073-$0.086 per gallon) giving a cost of 3-4 ore ($0,0086-$0.011) per litre ($0.04-$0.05 per gallon). The patentee, however, claims 5 ore ($.014) per litre (equivalent to $0.064 per gallon) license.

Chem.-Ztg. vol. 35 (1911) p. 286.
Wochbl. Papierfabr. vol. 42 (1911) p. 1440.
Chem. Abs. vol. 5 (1911) p. 2942.

MANUFACTURE OF ALCOHOL FROM SULPHITE-WASTE LYES.

Description of Wallin's process under the following headings:—

(1) Composition of the lye, (2) Neutralization of the lye, (3) Graduation of the lye, (4) Separation of the lime, (5) Preparing the yeast, (6) The fermentation, (7) Results of fermentation, (8) Separating off the yeast, (9) The distillation and apparatus, (10) The sulphite lye after distillation, (11) Pollution of rivers by the lye after alcohol distillation, (12) Cost of manufacture.

Most of the figures given are based on alcohol plant at Kopmanholmen. For a 12,000-ton mill the cost of alcohol is given as

A 720,000 litre production, 2·83 cents per litre of 100 per cent alcohol.
B 840,000 litre production, 2·53 cents per litre of 100 per cent alcohol.

If the profit from the reclaimed sulphur and lime which can be calculated to about 1·6 – 1·87 cents per litre of alcohol is also taken into consideration the actual cost of 1 litre of alcohol will be about 1 cent for 100 per cent alcohol.

Pulp Paper Mag. Can. vol. 10 (1912) p. 358.

Forrester, G. P.—THE RECOVERY OF WASTE SULPHITE LIQUORS.

Discusses Ekstrom's and Wallin's processes with regard to yield and costs.

Paper vol. 6 (1912) No. 11 p. 15.

PRODUCTION OF SULPHITE SPIRIT IN SWEDEN.

The yearly production of spirit in three Swedish mills will now be 3,000,000 litres (660,000 gallons) which will be denatured with benzol.

Papier-Fabr. vol. 9 (1911) p. 618.

COST OF SULPHITE SPIRIT.

From one metric ton (2,204 lb.) of pulp 60-80 litres (13·2-17·6 gallons) of spirit can be manufactured at a cost of 17-18 pfennigs ($0.04-$0.043) per litre, equivalent to $0.182-$0.195 per gallon. The selling price is 45-50 pfennigs ($0.107-$0.119) per litre, equivalent to $0.486-$0.54 per gallon.

Papier-Ztg. vol. 36 (1911) p. 937.

Landmark, H. B.—UTILIZATION OF WASTE SULPHITE LIQUOR.

The lye is concentrated with an excess of an acid which forms with lime an insoluble salt, neutralized with an insoluble salt, drawn off after the precipitate has settled, and evaporated to 30° Bé. The product can be used as a ferment or as a glue for paper material.

Norwegian Patent 21848 (1911).
Chem. Abs. vol. 6 (1912) p. 2316.

MANUFACTURE OF SULPHITE SPIRIT IN SWEDEN.

The problem of using the spirit for motors is not yet solved. The manufacture of sulphite spirit does not develop as rapidly as was expected, as its uses are still very limited.

Wochbl. Papierfabr. vol. 43 (1912) p. 4829.

SULPHITE SPIRIT IN SWEDEN.

Uddeholms Aktiebolaz has built a motor car driven by sulphite spirit. It is hoped that it will be possible to utilize sulphite alcohol in the manufacture of artificial rubber.

Papier-Ztg. vol. 36 (1912) p. 1856.

Ljungberg, E. J.—SULPHITE SPIRIT.

The sulphite spirit is now purer than crude spirit from grain and nearly as pure as fine spirit.

Sweden could with her yearly production of 700,000 metric tons (770,000 short tons) sulphite pulp (1912) produce 60 million litres (3,200,000 gallons) of normal spirit (50 per cent). The wholesale prices are 50 ore ($0.134) per litre, equivalent to $0.61 per gallon for grain spirit, 30 ore ($0.084) per litre equivalent to $0.365 per gallon for potato spirit, and 25 ore ($0.067) per litre, equivalent to $0.304 per gallon, for sulphite spirit; therefore it cannot compete at the present time with benzine, in Sweden.

Affars varlden (1912) p. 133.
Papier-Ztg. vol. 36 (1912) pp. 337, 490.

Wallin, J. H.—ALCOHOL FROM WASTE SULPHITE LIQUOR.

For one metric ton (2,204 lb.) air-dry sulphite pulp 186.4 litres (41 gallons) of spirit (50 per cent) can be manufactured. In practice, however, only 120 litres (26.4 gallons) per metric ton (2,204 lb.) pulp are obtained.

Papier-Ztg. vol. 36 (1912) p. 1283.

Aktiebolaget Ethyl, Sweden.—TREATMENT OF WASTE SULPHITE LIQUOR FOR FERMENTATION.

The lactic acid formed in the fermentation vat sets sulphurous acid free, injuring the fermentation enzymes. After neutralization with lime (the liquor must be kept slightly acid during the fermentation) the waste liquor is treated with ammonia or ammonium salts. These are thereby transformed into amido-compounds, which are more valuable as nutriment for the enzyme than the ammonium salts. Previous to the aeration and fermentation oxidizing salts of manganese, chromium or cobalt are added to the boiling liquor, which is afterwards aerated with compressed air at 90°-95° and at last in a coke tower at 25°-35° C.

French Patent 446717 (1912).
French Patent 446718 (1912).
Chem.-Ztg. vol. 37 (1913) Rep. p. 116.
J. Soc. Chem. Ind. vol. 32 (1913) pp. 133 377.
Chem. Abs. vol. 7 (1913), pp. 1972, 2115.

Ekstrom, G.—ALCOHOL FROM WASTE SULPHITE LIQUOR.

The SO_2, which has a deleterious effect upon the fermentation, is counteracted by adding to the mass, before fermentation, an NH_4 salt and a neutralizing agent.

Swedish Patent 34623 (1912).
Chem. Abs. vol. 8 (1914) p. 1669.

Ekstrom, G.—PURIFYING ALCOHOL FROM WASTE SULPHITE LIQUOR.

The alcohol is freed from SO_2 and aldehyde compounds by treating the alcohol vapour (during distillation) with a solution of soda, to fix the SO_2 and decompose the aldehyde compounds.

United States Patent 1095830 (1912).
Canadian Patent 142290 (1912).
Chem. Abs. vol. 8 (1914) p. 2251.
Paper vol. 14 (1914) No. 22 p. 20.

Ekstrom, G.—ALCOHOL FROM SULPHITE LIQUOR.

The waste liquor from the sulphite-pulp process is treated with calcium carbonate (or similar material) and ammonium sulphate to neutralize free sulphurous acid, to convert organic compounds loosely combined with sulphurous acid into compounds innocuous to the subsequent fermentation, and to increase the quantity of nitrogenous matter in the liquor.

United States Patent 1042332 (1912).
Canadian Patent 142288 (1912).
J. Soc. Chem. Ind. vol. 31 (1912) p. 1075
Paper vol. 10 (1912) No. 9 p. 16.

Ekstrom, G.—ALCOHOL FROM SULPHITE LIQUOR.

Urine is added to the sulphite liquor to be fermented.
United States Patent 1046160 (1912).
Canadian Patent 142289 (1912).
J. Soc. Chem. Ind. vol. 31 (1913) p. 103.
Chem. Abs. vol. 7 (1913) p. 677.
Paper vol. 10 (1912) No. 9 p. 16.

Wallin, J. H.—THE RECOVERY OF WASTE SULPHITE LIQUOR.

Mill at Kopmanholmen. Annual production of sulphite pulp 12,000 tons; daily yield of alcohol 520 gallons. Cost of production in Sweden said to be 11·2 cents per gallon. Expenses lower when large quantities of waste liquor are treated under special conditions. Cost of pulp reduced $2.65 per ton by manufacture of alcohol as a by-product. Alcohol only useful as fuel.

Pulp Paper Mag. Can. vol. 11 (1913) p. 526.

Ekstrom, G.—ALCOHOL FROM SULPHITE LIQUOR.

As a preparatory step to the manufacture of alcohol by the fermentation of the saccharine matters of sulphite wood-pulp liquors, a catalyst for oxidation (e.g. a salt of pure Mn. Cr. or Co) and a base (e.g. CaO) are added to the liquor which is aerated while in a hot state; the solid matters are then separated, and the liquor is cooled and again aerated while cold before fermentation.

United States Patent 1050723 (1913).
Swedish Patent 34624 (1912).
Canadian Patent 142287 (1912).
J. Soc. Chem. Ind. vol. 32 (1913) p. 192.
Chem. Abs. vol. 7 (1913) p. 889, vol. 8 (1914) p. 1669

Landmark, H. B.—UTILIZING FERMENTABLE CARBOHYDRATES IN SULPHITE LYES.

The sulphite liquor is treated with skimmed milk and dilute sulphuric acid, heated until casein is precipitated, and filtered. The filtrate is treated with more sulphite liquor and sulphuric acid, and heated in order to hydrolyze the lactose. The product may be used as a reducing agent or neutralized and fermented. Whey may be substituted for skimmed milk and is added to the whole of the sulphite liquor at once, since no casein is precipitated.

French Patent 456871 (1913).
Norwegian Patent 23673 (1912).
J. Soc. Chem. Ind. vol. 32 (1913) pp. 1063, 488.
Chem. Abs. vol. 8 (1914) p. 822.
Papir J. vol. 1 (1913) p. 15.
Paper vol. 13 (1914) No. 18 p. 17.

Walker, W. O.—THE PROBLEM OF THE WASTE LIQUOR FROM SULPHITE PULP-MILLS.

It has been calculated that nearly two per cent of the organic material of the liquor is fermentable by yeast. The process is essentially as follows:—

The acid of the liquor is nearly neutralized with lime, the liquor is then aerated, and the lime sludge, consisting of calcium sulphate and part of the organic matter, is removed. The clear liquid is now treated with a special yeast cultivated for the purpose and a weak current of air is blown through the liquid during the fermenting period. The fermentation is completed after four to six days. Upon distillation 1·2 per cent of alcohol by volume is obtained. The raw alcohol contains cymol, methyl alcohol, acetone, and acetaldehyde as impurities. There is considerable doubt in regard to the market for the large amount (of such a grade) of alcohol that could be made from such a tremendous supply of raw material. Further, since only about 2 per cent of the organic material is utilized, the process does not completely solve the problem of its disposal.

J. Soc. Chem. Ind. vol. 32 (1913) p. 389.
(See "General" p. 185.)

Ekstrom, G.—TRANSFORMATION OF CELLULOSE INTO FERMENTABLE SUGARS.

Waste liquor is used for dilution in the transformation of cellulose into sugars, in order to heat and partly neutralize the acid. After the hydrolysis a new quantity of liquor is added in order to neutralize the free acid still present.

Swedish Patent 33876.
Chem.-Ztg. vol. 37 (1913) Nos. 31 and 32.

Ekstrom, G.—THE ALCOHOL LEGISLATION.

A general introduction of sulphite-spirit manufacturing is made difficult by the legislation in Sweden.

Svensk. Pap. Tid. (1913) p. 2258.
Papir J. (1914) p. 298.
Papier-Ztg. vol. 35 (1910) p. 3244 and vol. 38 (1913) p. 2258.

Aktiebolaget Ethyl and Ekstrom, G.—APPARATUS FOR FERMENTATION OF LARGE QUANTITIES OF DILUTE SUGAR SOLUTIONS, ESPECIALLY WASTE SULPHITE LIQUORS.

Austrian Patent Application 940 (1913).
Swedish Patent 35232 (1912).

Foth, G.—THE MANUFACTURE OF ALCOHOL FROM WOOD.

Considerably more spirit can be obtained from saw-mill wastes than from waste sulphite liquor.

Chem.-Ztg. vol. 37 (1913) p. 1221.

Ekstrom, G.—THE PRESENT SITUATION OF THE SULPHITE SPIRIT PROBLEM.

The alcohol is still too expensive for motors. The value of the spirit from one cub. m. (220 gallons) of waste liquor is kr. 2.40 ($0.643). The value of the heat obtainable from 1 cub. m. (220 gallons) is at a maximum kr. 1.00 ($0.268).

Svensk. Pap. Tid. (1914).
Papier-Ztg. vol. 39 (1914) p. 269.
Wochbl. Papierfabr. vol. 45 (1914) p. 825.

THE PRESENCE OF METHYL ALCOHOL IN SULPHITE SPIRIT.

The sulphite spirit contains methyl alcohol. It is possible to separate the two alcohols by distillation, but the process does not seem to be economical as the steam requirements are very high.

Papier-Fabr. vol. 12 (1914) p. 947.

Ekstrom, G.—PURIFICATION OF ALCOHOL FROM SULPHITE LYES.

Sulphite lyes and other liquids obtained by boiling cellulose materials with acid liquids are neutralized with a heavy, solid, neutralizing agent preparatory to further treatment for the production of alcohol. The solid neutralizing agent is added to the liquor in a vessel provided with a conical bottom, at the apex of which is a nozzle having helical passages. Air under pressure is supplied to the nozzle, whereby a spiral jet of air, entraining the solid reagent, is forced upward through the liquor. The neutralized liquor is drawn off near the surface through a siphon pipe supported by a float. Water under pressure may be forced through the nozzle, when desired to flush the bottom of the vessel, the flush water being drawn off through a pipe in axial alignment with the nozzle.

United States Patents 1098561 and 1098562 (1914).
Canadian Patents 142285 and 142286 (1912).
J. Soc. Chem. Ind. vol. 33 (1914) p. 785.
Chem. Abs. vol. 8 (1914) p. 2803.

Ekstrom, G.—NEUTRALIZATION OF ACID LIQUORS.

Limestone is used and a thorough mixing is effected by compressed air in a special apparatus.

Swedish Patent 35706 (1912).
Papier-Fabr. vol. 12 (1914) p. 727.

Ekstrom, G.—SULPHITE ALCOHOL IN SWEDEN.

In 1912 about 4,500,000 litres (990,000 gallons) of alcohol of normal strength were produced in three Swedish mills. The producers sell to the alcohol trust at 6⅔ cents per litre ($0·30 per gallon) absolute alcohol. Production is limited by faulty methods of distribution which make the retail price too high.

Svensk. Teckn. Tid.
Pulp Paper Mag. Can. vol. 13 (1915) p. 68.
Chem. Abs. vol. 9 (1915) p. 1114.

Landmark, H. B.—PROCESS OF MANUFACTURING ALCOHOL FROM WASTE SULPHITE LIQUOR.

Previous to the neutralization and the fermentation about one-sixth of the volume of the liquor is evaporated, preferably in vacuo.

Norwegian Patent 24562 (1914) Addition to 23673.
Tidschrift vol. 4 (1914) p. 222.
Papir J. vol. (1914) p. 186.

METHYL ALCOHOL FROM THE SULPHITE PROCESS (BERGSTROM'S PROCESS).

Installed in Sundsvall Cellulose Aktiebolag, Sundsvall, Sweden. The relief gases contain in the last period of the cook essential oils and methyl alcohol. Price of methyl alcohol 50 ore ($0·134) per kilogramme ($0·061 per lb.) and with large market. The gas is conducted through condensation columns and by alternating distillation and condensation a pure product of 95 per cent is obtained. The process is continuous. In a 20,000 metric ton (22,000 short ton) mill (easy bleach), 40,000 kilogrammes (88,000 lb.) of methyl alcohol were produced, giving a total profit of kr. 20,000 ($5,360). The cost of operation was kr. 5,700 ($1,528), which gave a net profit of kr. 14,300 ($3,832). This included depreciation and maintenance of plant amounting to kr. 8,000 ($2,144). The removal of essential oils and methyl alcohol also causes an improvement of the liquor.

Papir J. vol. 2 (1914) p. 56.

Aktiebolaget Ethyl.—PROCESS AND APPARATUS FOR FERMENTING LARGE QUANTITIES OF SOLUTIONS OF LOW SUGAR CONTENT, CHIEFLY WASTE SULPHITE LIQUOR.

Norwegian Patent 24757 (1914).
Papir J. vol. 2 (1914) p. 263.

Landmark, H. B.—ALCOHOL FROM WASTE SULPHITE LIQUOR.

According to Landmark's process the liquor is evaporated to five-sixths or seven-eighths of its original volume, whereby SO_2 is removed. The original liquor contains per 100 c.c. 2.27 grammes of sugar as dextrose; when concentrated, and after the addition of 0·33 per cent whey and neutralization with 2 grammes $CaCO_3$ per 100 c.c., the wash contains 2.61 grammes of sugar. To 100 litres (22 gallons) of liquor about 500 c.c. (0.11 gallons) of waste brewers' yeast is added. The yield is 1·27 per cent by volume or assuming that 0·01 per cent originates from the milk sugar the liquor yields 1·26 per cent of alcohol. Wallin's and Ekstrom's methods yield 0·95-1·05 per cent.

The manufacturing cost of alcohol in a mill producing 15,000 metric tons (17,000 short tons) of dry pulp, calculated on a yield of 1·2 per cent of alcohol by volume from the liquor and a recovery of 6 or 7 cub. m. (1,320-1,540 gallons) of liquor per metric ton (2,204 lb.) of pulp, is 9·68-8·72 ore ($0.026-$0.023) per litre of 100 per cent alcohol, ($0.118-$0.105 per gallon).

The use of denatured spirit for varnishes, lighting, etc., is increasing rapidly. The tax in Norway on 100-per-cent spirit is now 10 ore ($.0268) per litre ($0.122 per gallon).

Papir J. vol. 2 (1914) p. 63.
Pulp Paper Mag. Can. vol. 12 (1914) p. 267.

Ekstrom, G.—THE SULPHITE ALCOHOL PROBLEM.

The organic substances of waste liquor consist of 1·6-2·0 per cent of fermentable sugar, 6-7 per cent of precipitable substances, and 2·4-2·5 per cent of other organic substances.

The liquor, therefore, contains on an average per cubic metre (220 gallons): 18 kilogrammes (34·6 lb.) of fermentable sugar, 65 kilogrammes (143 lb.) of precipitable organic substances, and 24·5 kilogrammes (53·4 lb.) of other organic substances.

If transformed into alcohol the fermentable sugar has value of kr. 2·38 ($0.638). The precipitable substances used as fuel have the value of kr. 1·3 ($0.348) per cubic metre (220 gallons). The sugar should, therefore, always be utilized before precipitation.

Swedish legislation does not permit of the operation of distilleries producing taxable spirit for more than seven months yearly (October 1 to May 1) and the maximum production allowed is 600,000 litres (132,000 gallons) of 50 per cent alcohol. Denatured spirit may be manufactured in any quantity during the whole year. Most of the sulphite mills would produce 2,000,000 litres (440,000 gallons) of 50 per cent alcohol per year and would accordingly have to denature it all.

The mills are now depending on a company which handles the whole alcohol production of Sweden. This company buys 50 per cent alcohol from the mills for 12·5 ore ($0.0335) per litre ($0.152 per gallon) and sells it for 16-17 ore ($0.043-$0.046) per litre, equivalent to $0.195-$0.21 per gallon. The retail price for 90-95 per cent alcohol is 40-75 ore ($0.107-$0.20) per litre ($0.486-$0.91 per gallon) and for 50 per cent alcohol 21-39 ore ($0.0563-$0.105) per litre ($0.256-$0.477 per gallon). Crude 50 per cent spirit from potatoes is paid for by the company at a price of 86-88 ore ($0.23-$0.236) per litre ($1.05-$1.07 per gallon), that is 176 per cent of the price the sulphite-mills obtain. If the mills were allowed to produce 600,000 litres (132,000 gallons) taxable 50 per cent alcohol, they could afford to sell technical spirit without loss and be independent of the refining plants.

Papir J. vol. 2 (1914) p. 298.

Landmark, H. B.—UTILIZATION OF WASTE SULPHITE LIQUOR CHIEFLY WITH REGARD TO THE MANUFACTURE OF ALCOHOL.

Description of Landmark's process and comparison with the Swedish method. The Wallin-Ekstrom process yields 0·7-0·95 per cent of alcohol by volume. A "tempered" yeast is used. For neutralization 11-13 grammes of CaO are used per litre (0·11-0·13 lb. per gallon). In Landmark's process ordinary brewers' yeast can be used after addition of milk or whey and only 2-3 grammes of $CaCO_3$ are used per litre (0·02-0·03 lb. per gallon) for neutralization. Lignocasein is obtained as a by-product.

In case of a yield of 1·1 per cent by volume and a recovery of 6·5 cubic metres (1,430 gallons) of liquor per metric ton (2,204 lb.) of pulp the manufacturing cost of one litre of 100 per cent alcohol is 8·5 ore ($0.0228) which is equivalent to $0.104 per gallon. This calculation includes depreciation and improvements and assumes a mill producing 15,000 metric tons (17,000 short tons) of pulp. With the cost of handling, etc., the total cost of one litre is 10 ore ($0.0268) equivalent to $0.122 per gallon against 13-14 ore ($0.035-$0.375) equivalent to $0.16-$0.17 per gallon in the Swedish process.

The residual liquor from the distillation can be worked up for fuel according to Strehlenert's process. This is not possible with the liquor from the Swedish process, due to the nature of the precipitate caused by the high lime content.

Papier-Ztg. vol. 40 (1915) pp. 495, 519.
Wochbl. Papierfabr. vol. 46 (1915) p. 834.
Chem.-Ztg. vol. 39 (1915) p. 98.
J. Soc. Chem. Ind. vol. 34 (1915) p. 275.
Chem. Abs. vol. 9 (1915) p. 2709.
Paper vol. 16 No. 11 (1915) p. 18.

Marchand, C.—PROCESS OF TREATING BY-PRODUCTS LIQUORS FROM WOOD SULPHITE PLANTS TO PRODUCE ALCOHOL.

Sulphuric acid is added to the waste sulphite liquor and the major portion of the sulphur dioxide recovered while evaporating the liquor under vacuum. The remaining traces of sulphurous acid are oxidized (e.g. by the addition of a "peroxide material," $K.MnO_4$, H_2O_2, O_3) the acidity of the liquor is neutralized by lime, and the clear liquid decanted, after settling, and fermented to produce alcohol.

United States Patent 1155256 (1915).
J. Soc. Chem. Ind. vol. 34 (1915) p. 1087.
Chem. Abs. vol. 9 (1915) p. 3358.

Marchand, C.—RECOVERING BY-PRODUCTS FROM THE RESIDUE OF WOOD SULPHITE PLANTS.

The SO_2 is expelled and the remaining acids in the liquor are neutralized with an alkali. The liquor is decanted and fermented and the alcohol distilled. To the residue, comminuted fuel is added and mixed, the mixture evaporated and pressed into briquettes and dried.

Canadian Patent 163400 (1915).
See United States Patent 1155256 (1915).
Chem. Abs. vol. 9 (1915) p. 2980.

Landmark, H. B.—PROCESS FOR UTILIZING THE FERMENTABLE AND REDUCING CARBOHYDRATES IN SULPHITE-CELLULOSE WASTE LYES FOR OBTAINING ALCOHOL OR A REDUCING AGENT.

Addition to French Patent 456871 (1913).
J. Soc. Chem. Ind. vol. 34 (1915) p. 488.

E. Trainer's Heirs.—UTILIZATION OF SULPHITE-CELLULOSE BACK WATER.

German Patent 283931 (1911).
(See "Fertilizer" p. 141.)

ALCOHOL AND BENZOL FOR AUTOMOBILES.

According to v. Low experiments with a 1,360 kilogramme (2,990 lb.) motor car with 14 metric H.P. (13.8 English H.P.) motor gave the following results:—

Kind of Fuel.	Km. per Litre.	Miles per Gal.	Price per Litre.	Price per Gal.	Km. per Mark.	Miles per dollar.
	Km.	Miles.	Pf.	$	Km.	Miles.
Benzine alone	5·8	16·4	38·0	0·41	15·7	40·0
Benzol alone	7·1	20·0	37·5	0·406	18·9	44·3
1 part benzol + 1 part alcohol	7·5	21·2	35·8	0·388	20·9	54·5
1 part benzol + 2 parts alcohol	7·2	20·3	35·2	0·38	20·4	53·5
1 part benzol + 3 parts alcohol	7·0	19·8	34·9	0·378	20·0	52·4
1 part benzol + 4 parts alcohol	6·6	18·6	34·7	0·376	19·0	49·5
1 part benzol + 5 parts alcohol	6·0	16·95	35·5	0·384	17·3	44·2
Alcohol alone	5·4	15·25	34·0	0·368	15·8	41·4

The prices given are those that were fixed shortly after the beginning of the war.
Papir J. vol. 3 (1915) p. 238.

Onsager, G. T.—ALCOHOL FERMENTATION OF WASTE LYES.

The waste lye is subjected to alcoholic fermentation in presence of a yeast nutriment derived from milk sugar and made, for example, in the following manner: 1 litre of lye mixed with 1 litre of skimmed milk is slightly acidified with sulphuric acid and heated to about 50°C., the precipitate of casein and lignin compound is removed by filtration and the filtrate mixed with 299 litres of the waste lye. The mixture is boiled until about one-sixth of its volume has evaporated and the milk sugar is hydrolyzed; the liquor is then neutralized with calcium carbonate, cooled to 28°C., and sown with waste brewers' yeast in the proportion of about 400 c.c. per 100 litres (0.4 gallons per 100 gallons).

English Patent 24738 (1913).
(See Landmark's Patent p. 116.)
J. Soc. Chem. Ind. vol. 34 (1915) p. 25.
Chem. Trade J. vol. 56 (1915) p. 355.
Paper vol. 15 (1914) No. 21 p. 21 vol. 16 (1915) No. 7 p. 12.

THE SULPHITE-SPIRIT PROBLEM IN SWEDEN.

The cost of production of one litre of 100 per cent sulphite alcohol is on an average for the whole country 18.5 ore ($0.05) equivalent to ($0.227 per gallon). One litre of ordinary denatured alcohol from this will cost 20.5 ore ($0.055) equivalent to ($0.25 per gallon), and motor spirit denatured with benzol and one-half of ordinary denaturing substance about the same. Motor fuel consisting of 100 parts of spirit and 20 parts of benzol will require a price of 19.5 ore ($0.0522) equivalent to $0.237 per gallon. Alcohol can not compete with the cheap mineral oils used in the Diesel motor and crude-oil motors but can replace benzine in automobiles and motor-boats.

The price of ordinary denatured alcohol is calculated to 19·5 ore ($0.0522) per litre, equivalent to $0.237 per gallon and would have the same economic value as benzine at a gross price of 30 ore ($0.084) per litre or $0.365 per gallon. If denatured with benzol the proportion would be that a price of 19.6 ore ($0.0525) per litre ($0.239 per gallon) of alcohol corresponds to a price of 27 ore ($0.0724) per litre ($0.326 per gallon) of benzine. The alcohol, therefore, cannot compete with benzine before the price of benzine is fixed at 27 ore ($0.0724) per litre ($0.326 per gallon) c.i.f. harbour. This would mean an increase in the operating cost of automobiles of 7·2 per cent. By special construction of the engine the increase in operating cost would amount to only 1-2·6 per cent.

Alcohol is not economical for lighting purposes at this price. The Board of Trade proposes a protective import duty of 14 ore ($0.0375) per litre ($0.171 per gallon) of benzine.

Papir J. vol. 4 (1916) p. 44.

KIBY, W.—SULPHITE-PULP WASTE LYES AND THEIR UTILIZATION FOR THE PRODUCTION OF ALCOHOL.

The manufacture of alcohol from waste sulphite liquor according to Wallin's and Ekstrom's and Landmark's processes is discussed. Strehlenert's and Rinman's processes for manufacture of fuel are also reviewed. The author reaches the conclusion that the manufacture of alcohol from the lye must form the nucleus of any successful utilization, and that the recovery of other useful products must be made subsidiary to that object. With 8-10 parts of lye to 1 part of cellulose the fermentable sugars are at a concentration of 1-1·5 per cent and the unfermentable sugars at 0·5 per cent concentration. A higher yield than 88 litres (19·4 gallons) of 100 per cent alcohol per metric ton (2,204 lb.) cellulose can hardly be expected. Calculations may be based on 80 litres (17·6 gallons). Points of fundamental importance are that the free SO_2 must be expelled by heating, preferably in connection with a concentration of the lye, to about two-thirds its volume. The concentrated lye should be nearly neutralized with waste lime and the sludge removed, the final acidity being adjusted to the equivalent of 0·025 per cent H_2SO_4. It is imperative that complete attenuation should be effected with 24 hours fermentation. For this the yeast must be acclimatized to the lye and brought to the most active condition by preparation. Attenuation must be stimulated by continuous removal of CO_2 and by keeping the yeast in active suspension. A triple effect evaporating apparatus is described in which the first and second effects are used for concentrating the lye and the last effect for concentrating the spent wash from the distillation. A distilling plant is described, capable of treating 15,430 litres (3,400 gallons) of wash per hour, producing rectified spirit of 97 per cent strength and the usual by-products, from washes used in the manufacture of bakers' yeast by the aeration process, containing no more alcohol than the fermented lye (0·77-1·05 per cent by volume). This plant showed a consumption per 100 litres (22 gallons) of wash, of 14-15 kilogrammes (30·8-33 lb.) of steam when producing rectified spirit and of 11·5 kilogrammes (25·3 lb.) when making crude spirit. The cost of manufacturing alcohol from sulphite lye is estimated at 10-15 shillings ($2.44-$3.65) per hectolitre ($0.11-$0.16 per gallon) of 100 per cent alcohol. The spent wash may be used for destructive distillation or for "cell-pitch", or fodder. From the manufacture of 500,000 metric tons (550,000 short tons) of sulphite pulp in Germany it is calculated that 400,000 hectolitres (8,800,000 gallons) of alcohol could be produced annually.

Chem.-Ztg. vol. 39 (1915) pp. 212, 261, 284, 350.
J. Soc. Chem. Ind. vol. 34 (1915) p. 1085.
Chem. Abs. vol. 10 (1916) p. 116; vol. 9 (1915) p. 2311.
Paper vol. 17 (1915) No. 15 p. 12.

Hagglund, E.—DIE SULFITABLAUGE UND IHRE VERARBEITUNG AUF ALKOHOL (WASTE SULPHITE LIQUOR AND ITS CONVERSION INTO ALCOHOL).

A discussion of the manufacture of alcohol from waste liquor.

Tr. Viemeg Sohn, Braunischweig, Germany (1915).

Ekstrom, G.—APPARATUS FOR FERMENTING SULPHITE-CELLULOSE LIQUOR.

The liquor is supplied centrally to a fermentation vat by a pipe, which is provided at its end with an extension having horizontal discharging arms of different lengths which rotate close to the bottom of the vat, the ends being bent so as to discharge the liquor tangentially. The liquor is drawn off from the vat below the level of the spent yeast by means of a horizontal pipe provided with a valve to close its inner end, and with a vertical pipe extending upwards above the level of the healthy yeast, and open at its upper end, so that, by means of two valved discharge pipes, either fermented liquor or spent yeast may be drawn off.

United States Patent 1139507 (1915).
Canadian Patent 142542, 142543 (1912).
J. Soc. Chem. Ind. vol. 34 (1915) p. 729.
Chem. Abs. vol. 8 (1914) pp. 2251, 2803; vol. 9 (1915) p. 1825.

Hedalen, J.—UTILIZATION OF SULPHITE WASTE LIQUOR.

Describes the Landmark and Rinman Process.

Pulp Paper Mag. Can. vol. 14 (1916) p. 176.
Paper vol. 18 (1916) No. 17 p. 15.
Chem. Abs. vol. 10 (1916) p. 2403.
(See Landmark p. 119.)

Oman, E.—NEUTRALIZATION AND FERMENTATION OF WASTE SULPHITE LIQUOR.

The author is of the opinion that a special cultivated yeast is not necessary and that aeration is of significance only in so far as it is capable of modifying the acidity of the liquor. Complete neutralization is not possible with calcium carbonate alone, the remaining acidity being equivalent to 0·05-0·06 N, varying with different lyes. Lime exerts only 40-50 per cent of its theoretical neutralizing power, apparently because some of it is precipitated with organic matter. The most favourable acidity for fermentation is that equivalent to 0·02-0·03 N. The best method is to add an excess of calcium carbonate, determining the acidity, and if it exceeds 0·03 N to add the calculated quantity of milk of lime.

Papier-Fabr. vol. 13 (1915) pp. 534, 553.
Z. angew. Chem. vol. 28 (1915) Rep. p. 564.
J. Soc. Chem. Ind. vol. 35 (1916) p. 172.
Chem. Abs. vol. 10 (1916) pp. 3158, 527.

MANUFACTURE OF SULPHITE SPIRIT IN SWEDEN.

The Swedish Board of Trade has submitted a report to the Swedish Government with proposals for encouragement of the use and manufacture in Sweden of sulphite spirit. The principle is laid down that the manufacture and sale of denatured spirit for the propulsion of motors and other technical purposes should be reserved as far as possible to the sulphite-spirit factories, whereas the manufacture of spirits for consumption is to be left to factories hitherto engaged in that manufacture. Sulphite-spirit factories should be permitted to manufacture denatured spirit without restriction and should have the exclusive right of denaturing with benzol. It is further proposed to protect the sulphite-spirit industry by levying on benzine a customs duty of 14 ore ($0.0375) per litre ($0.17 per gallon).

Board of Trade J. Jan. 27 (1916).
J. Soc. Chem. Ind. vol. 35 (1916) p. 192.
Paper vol. 18 (1916) No. 4 p. 15.
Chem. Abs. vol. 10 (1916) p. 2403.

Tartar, H. V.—PROPOSED METHOD FOR THE PROFITABLE UTILIZATION OF WASTE SULPHITE LIQUOR.

The method is claimed to have several advantages over Ekstrom's process, among others the fact that no special yeast is required. The liquor is treated with a quantity of dilute (1: 3) sulphuric acid equivalent to its content of total sulphurous acid, and is concentrated, preferably in vacuo, at a temperature not above 85° C. to half its bulk, the sulphur dioxide expelled being recovered. The concentrated liquor is treated with a small quantity of potassium permanganate (1/2 oz. to 500 gallons of original liquor) to oxidize any remaining sulphurous acid, is made neutral to litmus by means of lime, allowed to settle, and the clear solution acidulated with 0·1 per cent of sulphuric acid and fermented with brewers' yeast for 40-60 hours at 27° C., the liquid being kept agitated. The concentrated liquor contains about 6 per cent of fermentable sugar, and the yield of alcohol ranges from 0.76-0.86 per cent by volume of the original liquor. In a properly controlled plant a yield of 1 per cent of alcohol should be attainable. The residue after distillation is not noticeably toxic to fish.

J. Ind. Eng. Chem. vol. 8 (1916) p. 226.
J. Soc. Chem. Ind. vol. 35 (1916) p. 483.
Chem. Abs. vol. 10 (1916) p. 1268.
Paper vol. 17 (1916) No. 26 p. 14.

Oman, E.—SUGAR FORMATION AND PRODUCTION OF DARK COLOURATION IN THE SULPHITE PROCESS.

Chem.-Ztg. vol. 39 (1915) p. 820.
J. Soc. Chem. Ind. vol. 38 (1916) p. 172.
Chem. Abs. vol. 10 (1916) p. 3158.
Paper vol. 18 (1916) No. 1 p. 22.

Marchand, C.—ALCOHOL FROM WASTE SULPHITE LIQUOR.

Description of the preparations of the Kimberly-Clark Co. to make alcohol from waste sulphite liquor. Experimental plant to give 500 gallons per day, to cost $15,000. Using Marchand process.

Paper Trade J. vol. 62 No. 5 (1916) p. 201.
Paper vol. 17 (1916) No. 23 p. 24.

SULPHITE ALCOHOL IN SWEDEN.

According to Svensk Pap. Tid. the Swedish Pulp Manufacturers' Association has expressed the opinion that if the sulphite industry is to venture money in the erecting of alcohol plants it is necessary that the state guarantee a market and a market price which will secure depreciation and interest on the plant. Further suggestions.

Pulp Paper Mag. Can. vol. 15 (1917) p. 247.

Reilley, A. E. J.—NEW SULPHITE MILL IN SWEDEN.

At the Korsnas lumber mills work has begun on the erection of a plant to obtain sulphite spirit from sulphite lye. The yearly production will be 1,500,000 litres (334,000 Imperial gallons) and the plant will be the largest of its kind in Sweden. The Ekstrom process will be used.

United States Commerce Reports, No. 276 Nov. 24, 1917, p. 755.

Jernberg, A. V.—FERMENTATION OF WASTE SULPHITE LIQUOR.

The liquor is prepared for fermentation by the addition of a neutralizing agent and a suitable quantity of calcium cyanamide, previously treated with water or steam, corresponding to the need of nitrogen and the acidity of the lye.

United States Patent 1221058 (1917).
J. Soc. Chem. Ind. vol. 36 (1917) p. 561.
Chem. Abs. vol. 11 (1917) p. 1750.
Pulp Paper Mag Can. vol. 15 (1917) p. 719.

Aktiebolaget Ethyl.—ALCOHOL FROM WASTE SULPHITE LIQUOR.

The tendency of fermenting viscose to foam in the digesting vessel is overcome, wholly or in part, by freeing it from CO_2 by exposing it in a finely divided state to the action of air.

Norwegian Patent 27613 (1917).
Chem. Abs. vol. 11 (1917) p. 1903.
Pulp Paper Mag. Can. vol. 15 (1917) pp. 765, 788.

Aktieselskabet Sulfitsprit.—ALCOHOL FROM WASTE SULPHITE LIQUOR.

To the lye is added milk, skim milk or whey, then the mass is slightly acidulated, heated, the casein-lignin precipitate filtered off, acid is added to the filtrate, and the liquid heated to hydrolyse, cooled to fermenting temperature, and fermented with ordinary ferment.

Dutch Patent 1763 (1917).
Chem. Abs. vol. 11 (1917) p. 1300.
Pulp Paper Mag. Can. vol. 15 (1917) p. 541.

Klason, P.—THE SUGARS IN THE WASTE SULPHITE LIQUOR.

The chief constituents of spruce wood are cellulose 50 per cent, carbohydrates 15 per cent, lignin 30 per cent, protein 0.7 per cent, rosin and fat 3.3 per cent. The author is of the opinion that the fermentable sugar in the waste sulphite liquor originated from the carbohydrates. Analysis of the liquor gave the following sugars values calculated on dry wood: Glucose, 7.9 per cent; mannose, 2.5 per cent; galactose, 1.3 per cent; arabinose, 4.3 per cent; total, 16.0 per cent. Xylose is not contained in spruce, or at most only in small quantity. Glucose and mannose ferment more easily than galactose and are apparently perfectly fermented, as the yield of alcohol usually obtained from the waste liquor is on an average 1 per cent by volume (3.8 per cent of alcohol by weight calculated on the wood or 7.6 per cent of fermentable sugars calculated on the wood) and the highest yield obtained is 1.4 per cent alcohol by volume (corresponding to 10.6 per cent of fermentable sugars, calculated on the wood).

Svensk Pap. Tid. vol. 20 (1917) p. 176.
(See " Composition " p. 12.)

Leschly-Hansen, K.—SULPHITE LIQUOR AND ITS USE FOR THE PRODUCTION OF ALCOHOL.

Extract of Hagglund's book on this subject.
Papir J. vol. 5 (1917).

Oman, E.—PRECIPITATING ORGANIC SUBSTANCES CONTAINED IN SULPHITE SOLUTION.

The sulphite liquors either concentrated or not are treated with substances yielding the radicals NH_4, K, Na, Mg, or Ca, and Cl, SO_4, PO_4, and CO_3 in such proportions that the liquor does not become alkaline, preferably heating the liquor and separating the sugar by any preferred means.

French Patent 481917 (1917).
Pulp Paper Mag. Can. vol. 15 (1917) p. 1197.

Hagglund, E.—WASTE SULPHITE LIQUOR AND ITS CONVERSION INTO ALCOHOL.

This is a translation of "Die Sulfitablauge und ihre Verarbeitung auf Alkohol" by O. F. Bryant of the Pulp and Paper Division of the Forest Products Laboratories of Canada.

Pulp Paper Mag. Can. vol. 15 (1917) pp. 1125, 1157, 1185.
Paper vol. 21 (1917) No. 16 p. 11; No. 17 p. 16; No. 18 p. 13; No. 19 pp. 11, 20; No. 20 p. 15.

PRODUCTION OF ALCOHOL FROM SULPHITE WASTE LIQUOR.

A discussion as to whether it is the cellulose of the wood or the organic non-cellulose material, principally lignin, present in wood from which sugar is extracted. The sulphite lye contains in all 1·4 per cent of sugar of which 4 per cent is fermentable. Excessive temperatures and SO_2 prevent fermentation.

Paper Trade J. vol. 65 (1917) No. 13, p. 40.
Pulp Paper Mag. Can. vol. 15 (1917) p. 1118.

FUEL

The calorific value of wood varies with the different species within wide limits and for spruce is found to be about 8,825 B.T.U. A high-grade sulphite pulp develops about 7,740 B.T.U. Assuming the sulphite pulp to represent 50 per cent of the wood, the solid substance of sulphite liquor from one ton of pulp would theoretically represent about 19,820,000 B.T.U. or about 1,375 pounds of coal of 14,400 B.T.U. In order to be able to utilize these substances for fuel it is necessary to separate them from the liquor and this can be done in one of two ways, either by evaporation of the water or by precipitation of the solid substances. The waste liquor from one ton of pulp represents 2,000 gallons and if all this liquor could be separated from the pulp a considerable quantity of coal would be required for the evaporation of the liquor to dryness. In the manufacture of cell-pitch it was found that one ton of coal was required per ton of cell-pitch of 10 per cent moisture-content. But the cell-pitch having a calorific power of only about 6,300 B.T.U. as against 12,600-14,400 B.T.U. for coal the scheme of direct evaporation would mean a considerable loss in fuel value. If modern multiple effect evaporators could be used for sulphite liquors, a surplus in fuel corresponding to about 500 pounds coal might possibly be obtained if all the liquor were recovered. But this is impossible. Assuming a maximum of 1,000 gallons of liquor per ton of pulp an amount of fuel corresponding only to 250 pounds of coal could be obtained per ton of pulp. This figure might possibly be increased considerably by employing evaporators of high efficiency utilizing the vapours from the evaporating liquor.

The idea of Strehlenert's process for the recovery of fuel from waste sulphite liquor is based upon the decomposition of the sulphur compounds of the lignin with sulphuric acid at high temperature and pressure. The sulphuric acid is formed by oxidation of the free SO_2 by air or oxygen. The ash content of the fuel is decreased by a previous treatment of the liquor with sodium bisulphate whereby the calcium can be recovered as sulphate. Details of the process are contained in the abstracts of literature given below.

Since the first patents were granted Strehlenert has investigated and improved the process. It was noticed that the presence of small quantities of iron, zinc, manganese or other hydrogen-forming metals decreased the yield considerably and that a precipitation was almost impossible when as much as 0·004 per cent or more iron was present. According to the patent the oxidation begins at a comparatively low temperature whereas the decomposition takes place at a high temperature and pressure. By introducing the air at a higher temperature the oxidation and decomposition take place simultaneously, and so rapidly that the action of the metal is eliminated. In order to avoid oxidation of sulphurous acid during heating to the temperature of decomposition, relief gases from the sulphite-mill (containing SO_2) are introduced, so that a pressure of one or two atmospheres is secured from the beginning. The sulphuric acid is then formed at the critical temperature according to the equation $3\ SO_2 = 2\ SO_3 + S$, and theoretically no air is required. However, the introduction of air is always favourable as it causes the organic compound to precipitate in a coarser and more easily filtered form than without air. The sulphur formed according to this reaction sublimes and this as well as the excess of sulphurous acid which is set free during the decomposition of the sulphonic acid can be recovered. The relief gases also contain hydrogen sulphide which can be recovered and utilized in the pulp-mill. Under these working conditions only very little sulphuric acid is formed, so that after the reaction the liquor contains only from 0·2 to a maximum of 0·4 per cent total acid with 0·02 per cent free acid. When oxidation is allowed to take place at the early stage of process (at low temperature) the residual liquor contains up to 1·5 per cent sulphuric acid. A high sulphuric acid content is injurious to the autoclave and often makes the precipitate gelatinous and decreases its calorific value. It is therefore important that the oxidation take place as near the critical temperature as possible. According to the first method of operation the precipitation was effected by oxidation of SO_2 to SO_3. The free SO_2 present in the liquor (often only 0·1) was sufficient to introduce the reaction of decomposition of the lignin compound. The reaction of the inorganic substances is then:—

$$SO_2 + O = \text{or finally } 4\ CaSO_3 = 3\ CaSO_4 + CaS.$$

As copper autoclaves were used first copper oxide and finally copper sulphate were formed according to the following reaction:—

$CuSO_4 + CaS = CaSO_4 + CuS$, which gives with sulphuric acid $CuS + 2H_2SO_4 = CuSO_4 + SO_2 + S + 2\,H_2O$.

The action of the copper, therefore, is advantageous as it causes the direct formation of fresh quantities of SO_2, but this reaction, of course, is injurious to the autoclave and at the present time the autoclaves are made from iron and have a lead lining. The reaction in this case can be expressed by the following equations:—

$$4\ CaSO_3 = 3\ CaSO_4 + CaS$$

$$CaS + H_2SO_4 = CaSO_4 + H_2S.$$

The formation of hydrogen sulphide may be regarded as a disadvantage but the new process requires only 20 to 25 per cent of the air used in the former process. This means that the autoclave can be charged to 75 per cent of its volume with liquor, while formerly only 60 per cent of the autoclave volume could be utilized. With regard to the yield it was stated that only about 75 per cent of the total solids are precipitated, and Strehlenert concludes that the portion precipitated consists of compounds of sulphinic acid while the remaining 25 per cent which are only precipitated with difficulty are sulphonic acid compounds. According to Strehlenert the remaining 25 per cent can be obtained by the addition of peat to the liquor. In calculating the yield per ton of pulp Strehlenert assumes that 1,200 gallons of waste liquor will drain off per ton of pulp and that by employing diffusers 1,800 gallons can easily be recovered. It is a fact, however, that only about 740 gallons of liquor will drain off from the blow-pits per ton of pulp, although 800 gallons can probably be obtained if the draining is continued for a longer period. Assuming that 800 gallons are recovered and that the liquor contains on an average 11 per cent solid substances, 880 pounds of dry substance are present in the liquor from one ton of pulp, of which a maximum of $880 \times 0{\cdot}75 = 660$ pounds are precipitated, while $880 \times 0{\cdot}25 = 220$ pounds remain in the liquor and can be recovered by precipitation in the presence of small quantities of peat. Diffusers provided with suction pumps remove the water from the precipitate up to 35 per cent.

The ash content is about 17-18 per cent, if the liquor has not previously been treated with sodium bisulphate or has not been concentrated. The fuel, free from ash and water, develops on an average 12,240 B.T.U. If the fuel contains 50 per cent moisture the calorific value of the precipitate obtained per ton of pulp will amount to approximately 5,800,000 B.T.U., corresponding to about 400 pounds of coal of 14,400 B.T.U. This fuel-value will of course increase with the quantity of liquor which can be removed, and for 1,200 gallons per ton is equal to about 600 pounds of coal. In regard to the heat required in the process, according to Strehlenert, the heat developed in the reaction, should theoretically cover the heat requirements for raising the temperature of the liquor from 212°-392° F., but disregarding this the heat requirements in the process when autoclaves of 2,200 gallons capacity are used would be:—

Heating of the metal of the autoclave about 180° F., approximately 436,480 B.T.U.
Heating of 1,650 gallons liquor about 180° F., approximately 2,976,000 B.T.U.
Total heat requirement, 3,412,480 B.T.U.

This figure, however, represents the heat required for one single cook. When several autoclaves are combined so that the excess heat from one cook can be utilized in the other autoclaves at least 50 per cent of the heat is saved, and assuming an efficiency of 80 per cent for the boiler and a calorific value of 14,400 B.T.U. for the coal the heat required for 1,650 gallons of liquor will be:—

$$\frac{1706240 \text{ B. T. U.}}{14400 \times 0{\cdot}8} = 148 \text{ pounds coal}$$

or, for 800 gallons, 72 pounds, and for 1,200 gallons, 108 pounds coal. This gives an actual yield of fuel per ton of pulp corresponding to 328 or 492 pounds coal having a calorific value of 14,400 B.T.U., depending upon whether 800 or 1,200 gallons of liquor are recovered. An estimation of operating costs for the production of fuel is made by Strehlenert for a plant in Scandinavia operating 3 autoclaves of 2,200 gallons volume in handling the liquor from a yearly production of 17,000 metric tons (18,733 short tons) of pulp, assuming a recovery of 1,320 gallons of liquor per metric ton (1,200 gallons per short ton). The operating cost for one metric ton of fuel recovered is according to these calculations kr. 11.79 ($3.17) equivalent to $2.88 per short ton. This fuel however is of an inferior quality containing about 18 per cent ash and is generally used in a moist condition. Considering these two points the price of the fuel would be equivalent to a price of about $5.25 per metric ton of good coal of 14,400 B. T. U. ($4.75 per short ton). Strehlenert further assumes the most favourable concentration of the liquor, namely about 17 per cent solid substances, which is very near the concentration of the liquor obtained by indirect heating and forced circulation.

Assuming a concentration of 11 per cent the yield per autoclave charge will be considerably lower, and considering the higher cost of labour, etc., on this continent the price per ton of coal recovered will be $7 and $7.50 on the basis of a 30,000-metric-ton (33,075 short tons) mill and recovery of 1,320 and 880 gallons of liquor respectively per metric ton of pulp (1,200 and 800 gallons respectively per short ton).

The calculations are as follows: In case of 880 gallons of liquor per metric ton (800 gallons per short ton) of pulp, 726 pounds of fuel, equivalent to 440 pounds of coal (14,400 B.T.U.) are obtained per metric ton of pulp (660 pounds of fuel, equivalent to 400 pounds of coal per short ton). Eighteen per cent of this fuel is used in the process, leaving 361 pounds of coal as actual yield per metric ton (328 pounds per short ton). The fuel recovery from a 30,000-metric-ton (33,075 short tons) mill would therefore correspond to 4,920 metric tons of coal per year (5,425 short tons). Four autoclaves are required, and 7 men in 3 shifts for their operation. The cost of buildings is placed at $55,000 and the cost of apparatus at $89,000. Assuming a depreciation of the buildings of 10 per cent and of the apparatus of 15 per cent the operating cost for the production of one ton of coal (14,400 B.T.U.) will be:—

	Metric tons	Short tons
Depreciation of buildings	$1 12	$1 02
Depreciation of apparatus	2 71	2 46
Labour	3 17	2 87
Power	0 02	0 02
Repairs	0 50	0 45
Total cost per ton of coal	$7 52	$6 82

In case of 1,320 gallons of liquor per metric ton of pulp (1,200 gallons per short ton) fuel corresponding to 540 pounds of coal is obtained (492 pounds per short ton). Six autoclaves are required operated by 9 men in 3 shifts. The operating cost calculated as above is found to be about $7 per metric ton of coal ($6.35 per short ton). This very high cost might be considerably reduced by employing liquor from the Morterud process, which will increase the yield per autoclave as will also the addition of a small quantity (0.25-0.5 per cent) of peat in the decomposition process. The recovery of by-products such as acetone, acetic acid, formic acid, and methyl alcohol may also reduce the cost of the fuel considerably. Plans have been made to dry-distil the precipitate of organic substances, using the residual coke for fuel.

Very recently Landmark has proposed a modification of this process in which ozone is formed from the air in the upper part of the autoclave by an electric spark. The temperature and pressure required in the process should in this way be appreciably decreased. A discussion is at present going on between the two inventors which probably will lead to interesting results.

Dorenfeldt, L. J.—WASTE LYES FROM CELLULOSE MILLS.

The author claims that there is sufficient heat value in the organic substances of the waste liquor for evaporation and incineration and still a surplus of calorific power equal to about 58 kilogrammes (128 pounds) of good coal per cubic metre (220 gallons).

Papier-Ztg. vol. 23 (1898) p. 1652.
J. Soc. Chem. Ind. vol. 17 (1898) p. 788.

Dorenfeldt, L. J.—PROCESS FOR UTILIZING WASTE LIQUORS FROM THE MANUFACTURE OF PULP FROM WOOD, ESPARTO, ETC., AS A FUEL BY SPRAYING THROUGH NOZZLES.

The liquors are evaporated to such an extent (40°-50°Bé) that they can be atomized in a hot condition and after filtration.

German Patent 122489 (1898).
Austrian Privilegium 4602 (1898).
Papier-Ztg. vol. 26 (1900) part I p. 2602.
Chem. Zentr. (1900) part II p. 248.

Cremer, B. (from Dorenfeldt, L. J.)—APPARATUS FOR UTILIZING WASTE LIQUORS AS FUEL.

English Patent 11974 (1898).
J. Soc. Chem. Ind. vol. 18 (1899) p. 702.

Dorenfeldt, L. J.—HEAT VALUE OF WASTE LIQUORS FROM PULP MANUFACTURING.

Papier-Ztg. vol. 24 (1899).

Nemethy, E.—COMBUSTION VALUE OF WASTE SULPHITE LIQUOR.

Zentr. oesterr.-ung Papierind No. 18 (1903).
Papier-Ztg. vol. 28 (1903) p. 1897.

Trainer, E.—GAS AND COKE FROM SULPHITE LIQUOR.

The waste lyes are evaporated to dryness with the addition of compounds of the alkalies or alkaline-earths and of finely-divided lignite or low-grade coal, and the residue is formed into briquettes and carbonized. Claim is also made for the addition to the lyes of such substances as will produce slag during the carbonization process and thus render the coke stronger.

German Patent 181126 (1905).
Papier-Ztg. vol. 32 (1907) p. 994.
Wochbl. Papierfabr. vol. 38 (1907) p. 1307.
J. Soc. Chem. Ind. vol. 26 (1907) p. 1272.

Kayser, H.—PROCESS FOR EVAPORATING WASTE SULPHITE LIQUOR AND UTILIZING THE RESIDUES FOR FUEL.

Papier-Ztg. vol. 35 (1910) p. 768.

Stora Kopparbergs Bergslags Aktiebolag.—HUMUS-LIKE SUBSTANCES FROM SULPHITE LYES.

After the manufacture of alcohol from sulphite liquor or similar waste lyes from the treatment of cellulosic materials with acids, the residual liquor is treated with a basic substance, such as lime, to recover the humic substances; the amount of lime may be only sufficient to produce a feebly-alkaline solution, in which case its action may be intensified by passing air through the mixture after addition of a small quantity of an oxygen carrier, such as a manganese salt. The products may be used as fuel.

German Patent 256,964.
Papier-Ztg. vol. 37 (1913) p. 768.
Papier-Fabr. vol. 11 (1913) p. 342.
J. Soc. Chem. Ind. vol. 32 (1913) p. 421.
Chem. Abs. vol. 7 (1913) p. 2472.

Strehlenert, R. W.—PROCESS FOR OBTAINING THE ORGANIC AND INORGANIC CONSTITUENTS OF SULPHITE LIQUOR.

The sulphurous acid in the waste liquors is oxidized by heating in an autoclave to a high temperature under pressure, in presence of air or oxygen, whereupon the sulphuric acid formed precipitates the lignin substances. Before the oxidation process, a soluble acid salt such as sodium bisulphate (1·5-2·1 per cent) may be added to the waste lye. The precipitated substance may be used as a fuel, having a calorific value of 6,000-7,000 calories (10,600-12,600 B.T.U.) It is stated that the solution which remains is so free from solids that it can be safely run into any drain or stream.

Swedish Patent 34941 (1912).
Norwegian Patent 24140 (1912).
German Patent 266096 (1912).
Canadian Patent 151445 (1913).
United States Patent 1149420 (1915).
Papier-Fabr. vol. 9 (1913) p. 666.
J. Soc. Chem. Ind. vol 33 (1913) p. 1104, vol. 34 (1915) p. 957.
Chem. Abs. vol. 8 (1914) p. 572.
Paper vol. 17 (1915) No. 2 p. 19.
Paper Trade J. vol. 63 (1916) No. 19 p. 64.

Strehlenert, R. W.—UTILIZATION OF WASTE SULPHITE LYE.

Pulp Paper Mag. Can. vol. 11 (1913) p. 452.
Chem. Abs. vol. 7 (1913) p. 3022.

Strehlenert, R. W.—RECOVERY OF SO_2, $CASO_4$, AND FUEL FROM SULPHITE LYES.

The chief organic constituent of the waste lyes is the calcium salt of lignosulphonic acid; this is soluble in water and is decomposed in acid solution at a high temperature in presence of air, yielding sulphuric and sulphurous acids and insoluble lignin. It is necessary to regulate the temperature and quantity of air to avoid carbonization of the precipitated lignin on the one hand and its formation in a gelatinous condition on the other hand. Under suitable conditions the lignin is precipitated in a granular form, which is easily separated and dried for use as a fuel; this fuel has a heating value of 7,000 calories (12,600 B.T.U.) calculated on the ash-free substance. In order to obtain the lignin as free from ash as possible, the calcium should first be precipitated by sodium bisulphate. The hot lyes from the digesters are treated with 1.5-2 per cent of sodium bisulphate and the calcium sulphate is separated and dried for sale. The clear solution of sodium ligninsulphonate is charged into pressure vessels to about 60 per cent of their total capacity and heated to 100°C. Air is then forced in up to a pressure of about 18 atmospheres (270 lb.). The temperature rises about 20°C. as the result of the reaction and is slowly raised to 150°C. The sulphurous acid liberated from the lye is oxidized to sulphuric acid which induces the decomposition of the lignin salt between 160° and 170°C. After a temperature of 200°C. or higher has been reached, which should be in about 40-60 minutes measured from the time of starting from 100°C, digestion is finished. At the critical moment when decomposition sets in (160°-170°) the pressure in the vessel rises very rapidly and the sulphur dioxide is liberated and blown off through absorption towers for recovery. At the close of the heating period a feeble current of air must be blown through the liquid in order to granulate the precipitate. This air, together with the excess of steam, is utilized to heat the contents of a second digester. The precipitate of lignin is washed and drained in the centrifuge until it contains about 50 per cent of water. It may be dried further by a convenient source of waste heat but should retain 20 per cent of moisture when used for fuel, as when dry it burns too rapidly. From the manufacture of one metric ton (2,204 pounds) of cellulose about 10 cubic metres (2,000 gallons per short ton) of lye are obtained, containing, when the digestion is performed with indirect steam, 11.6 per cent of dry substance. From such a lye there were recovered 5-6 grammes of sulphur dioxide per litre, the original waste lye containing 8.6 grammes per litre. This corresponds to a recovery of 25-30 kilogrammes of sulphur per metric ton (2,240 lb.) of pulp (50-60 lb. per short ton). There were also obtained, with a heating of 65 minutes, 74 grammes of dried lignin precipitate per litre (0.74 lb. per gallon). The final waste liquor contained 0.19 per cent of sugars. The cost of treatment is estimated at about kr. 5 per metric ton (2,204 lb.) of lignin ($1.22 per short ton). The quantity of lignin recovered is capable of furnishing the whole of the fuel requirements of the pulp-mill. In addition there are obtained 140-150 kilogrammes of commercial calcium sulphate per metric ton (2,204 lb.) of cellulose produced (280-300 lb. per short ton).

Svensk Kem. Tid. vol. 25 (1913) p. 78.
Papier-Fabr. vol. 11 (1913) pp. 645, 666.
J. Soc. Chem. Ind. vol. 32 (1913) p. 652.
Chem. Abs. vol. 7 (1913) p. 2471.
Pulp and Paper Mag. Can. vol. 11 (1913) p. 778 vol. 12 (1914) p. 46.
Paper vol. 12 (1913) No. 9 p. 18.

Strehlenert, R. W.—SULPHUR FROM WASTE LIQUOR.

By Strehlenert's process a sulphite mill of 20,000 metric tons (22,050 short tons) production will save 100,000 kilogrammes (220,000 lb.) of coal, assuming a price of kr. 15 ($4.02) per metric ton ($3.65 per short ton) and a coal consumption of 0·5 ton per ton of pulp.

Svensk Kem. Tid. (1913) p. 78.
Chem.-Ztg. vol. 37 (1913) Rep. p. 605.
Wochbl. Papierfabr. vol. 44 (1913) p. 4142.
(See "Sulphur" p. 154.)

Strehlenert, R. W.—FUEL FROM WASTE SULPHITE LIQUOR.

Description of process.
Papier-Ztg. vol. 39 (1914) p. 414.

Ekstrom, G.—REMOVAL OF ORGANIC CONSTITUENTS FROM SULPHITE LIQUORS AFTER FERMENTATION.

United States Patent 1087356 (1914).

Briggs, J. F.—STREHLENERT'S PROCESS FOR TREATMENT OF SPENT SULPHITE LYES.

Description of Strehlenert's process.
Chem. World vol. 2 (1914) p. 346.
Chem. Abs. vol. 8 (1914) p. 1204.
Paper Maker Brit. Trade J. Annual No. 1913-14 p. 66.
Paper vol. 13 (1913) No. 11 p. 21.

Landmark, H. B.—UTILIZATION OF WASTE SULPHITE LIQUOR CHIEFLY WITH REGARD TO THE MANUFACTURE OF ALCOHOL.

The original liquor contains 60-80 grammes of lignin and small amounts of other organic matter per litre. (0·6-0·8 lb. per gallon). The liquor may be evaporated and cell-pitch obtained. The mash from the alcohol distillation is concentrated to 75 per cent of its original volume and contains approximately 115 grammes of dry substance per litre (1·15 lb. per gallon). One cubic metre (220 gallons) of waste liquor would then give 63·8 kilogrammes (140·3 lb.) of air-dry cell-pitch. This is equivalent to 57·4 kilogrammes (126.3 lb.) of absolutely dry cell-pitch as 37.6 kilogrammes (82·8 lb.) of cell-pitch are required for the evaporation of water from 1 cubic metre (220 gallons) of wash, and 20 kilogrammes (44 lb.) of sugar are removed in the fermentation process.

$$115-(20+37\cdot6)=57\cdot4$$ kilogrammes (126·3 lb.)

The heat value of cell-pitch is 3,500 calories (6,300 B.T.U.) With a heat value of 6,000 calories (10,800 B.T.U.) for coal 63·8 kilogrammes (140·3 lb.) of cell-pitch is equal to $\frac{63\cdot8\times3{,}500}{6{,}000}=37\cdot2$ kilogrammes (82·8 lb.) of coal.

If 10 cubic metres of liquor can be recovered from 1 metric ton (2,204 lb.) of pulp (2,000 gallons per short ton), 372 kilogrammes of coal of 6,000 calories (10,800 B.T.U.) is recovered from 1 metric ton (2,204 lb.) of pulp (742 lb. per short ton). But the cell-pitch contains all the organic substance of the liquor and may be used for other purposes as well.

Strehlenert's method is described. This gives the same result with the mash as with the original liquor.

Waste liquor gives by this process 60-90 grammes lignin substance per litre (0·6-0·9 lb. per gallon). In this no subtraction is made for fuel required. This would be less than the cell-pitch obtainable, as in the latter case all the organic substances are contained in the product.

Wochbl. Papierfabr. vol 46 (1915) p. 843.

Murbe, E.—FUEL FROM LIGNIN PRECIPITATED FROM SULPHITE LIQUOR.

Lignin is removed from the autoclave by rinsing with water and is freed from acid at the same time. The wet mass is dehydrated by filtering and treatment with hot flue-gases which are then directed against the furnace walls by means of a blower.

Swedish Patent 41542 (1916).
Chem. Abs. vol. 11 (1917) p. 535.

Kjaer, A. H. & Co.—DISINTEGRATING WASTE SULPHITE LIQUOR.

Indirect heating is combined with direct heating so that the temperature of the liquor is first brought, by indirect heating, to a point where disintegration products are precipitated on highly heated surfaces, whereupon heating is continued by direct steam.

Norwegian Patent 27637 (1917).
Chem. Abs. vol. 11 (1917) p. 1902.
Pulp Paper Mag. Can. vol. 15 (1917) p. 741.

METHOD FOR PRECIPITATING THE ORGANIC MATTER IN WASTE SULPHITE LIQUOR.

A new method for precipitating the organic substances is proposed by H. B. Landmark. The method is described and compared with Strehlenert's method. The two methods have the same principle, Landmark using ozone where Strehlenert used air or oxygen. The ozone is produced by means of electric sparks in the upper part of the autoclave. The pressure is hereby reduced to 10-14 atmospheres and no H_2SO_4 is required. Landmark uses a copper autoclave with a pressure of 2-5 atmospheres and a voltage of 10,000 volts. After 1 hour's boiling at 11 atmospheres the process was finished, and the black powder obtained yielded 60 grammes per litre of sulphite liquor. Instead of producing ozone in the autoclave it can be introduced into the autoclave at the required temperature and pressure.

Papir J. vol. 4 (1916) No. 22, p. 260.
Svensk Pap. Tid. (1916) No. 23 p. 25.
Pulp Paper Mag. Can. vol. 15 (1917) p. 88.

Landmark, H. B.—PRECIPITATING ORGANIC SUBSTANCES IN WASTE SULPHITE LIQUOR.

Waste sulphite liquor is reacted upon by H_2SO_4, produced in the liquor by oxidizing its SO_2 content with ozonized air formed by the discharge of electric sparks under pressure in the vessel containing the liquor. This effects the precipitation of organic substances, under a pressure of 6-7 atmospheres.

United States Patent 1236948 Aug. 14 (1917).
Chem. Abs. vol. 11 p. 2963.
J. Soc. Chem. Ind. vol. 36 (1917) p. 1092.

Landmark, H. B.—METHOD FOR PRECIPITATING ORGANIC MATTERS IN WASTE SULPHITE LIQUOR.

Answer by Landmark to Strehlenert: Landmark calls attention to the fact that Strehlenert in the demonstrations of his process has used 20 atmospheres pressure and 200°C. and that these figures are also used in the description of his Norwegian patent. Even when copper sulphate was used as a catalyst, a pressure of 20 atmospheres was necessary. Landmark says that a precipitation of the lignin is possible at 7-9 atmospheres (2 per cent of the liquor) and Landmark has at this pressure obtained a product which can easily be filtered and washed. The precipitate may in that case be a little carbonized and the yield somewhat lower but the lower yield is then balanced by the better quality of the product, the fuel value being higher. The yield depends on the amount of solid matter in the liquor. Analysis of liquor from one mill gave 100-123 grammes per litre. With 100 grammes of solid substance, the liquor contained chiefly 14 grammes of ash and 18 grammes of sugar per litre. The rest is chiefly lignosulphonic acid, and 60 grammes will be the maximum yield obtainable. Landmark obtained 60 grammes in a demonstration of his process. The gypsum in this test was previously removed with sodium sulphate. Landmark claims in his new patent the use of electric sparks for the ozonizing of the oxygen in the air.

Papir. J. vol. 4 (1916) No. 24 p. 279.
Pulp Paper Mag. Can. vol. 15 (1917) pp. 88, 101.

Strehlenert, R. W.—METHOD FOR PRECIPITATING ORGANIC MATTERS IN WASTE SULPHITE LIQUOR.

Answer by Strehlenert to Landmark: Strehlenert claims that the oxidation of SO_2 in his process takes place at a temperature a little higher than 100°C. and a very little above atmospheric pressure. The addition of H_2SO_4 is only required when autoclaves of other material than copper are used, and even then only if the SO_2 content of the liquor is very low or when the liquor had previously been neutralized. Strehlenert has, however, worked out a method by which even in such cases the small amount of H_2SO_4 (0·1-0·5 per cent) used for starting the reaction is made unnecessary. The oxidation from SO_2 to SO_3 with ozone has been closely studied by Strehlenert, who claims the method will be only of theoretical value. Even if the ozonization were practically possible the operation would hardly be cheaper than pressing some air into the autoclave and oxidizing at 4-5 atmospheres.

With Landmark's process 60 grammes of precipitate were obtained per litre of liquor but the ash content was not given. This must be 22 per cent if the liquor has not been previously treated. By decomposition of the same kind of liquor Strehlenert has obtained between 87 and 98 grammes per litre and with an ash content up to 7 per cent when using his own method.

Papir J. vol. 4 (1916) No. 23 p. 269.
Pulp Paper Mag. Can. vol. 15 (1917) pp. 101, 88.

Landmark, H. B.—Strehlenert, R. W.—METHOD FOR PRECIPITATING ORGANIC SUBSTANCES FROM WASTE SULPHITE LIQUOR.

In a continued discussion of the two processes Landmark makes the statement that with his process the oxidation of SO_2 to SO_3 can be effected at ordinary temperatures and pressures, and that the decomposition of the lignin compounds takes place at less than 12 atmospheres whereas Strehlenert uses 20 atmospheres in his process. Arrangements will now be made to demonstrate the two processes in presence of both inventors.

Papir J. vol. 5 (1917) pp. 36, 37.

Pulp Paper Mag. Can. vol. 15 (1917) p. 449 (See this magazine, vol. 15 [1917] pp. 88, 101, 140, 343).

Strehlenert, R. W.—PROCESS FOR PRECIPITATING ORGANIC SUBSTANCES IN WASTE SULPHITE LIQUOR.

In a continued discussion with Mr. Landmark (see Pulp Paper Mag. Can. vol. 14, 1916, p. 140) the statement is made that the oxidation of the SO_2 to SO_3 takes place, even when no ozone is present, at a low temperature and pressure (5-7 atmospheres). However, the critical temperature at which the decomposition of the liquor takes place is, under ordinary conditions, at about 190°-195° C. and at the corresponding steam pressure (14 atmospheres), but it is more economical to raise the pressure a little higher. It is possible to decompose the liquor at a lower temperature when the necessary amount of H_2SO_4 (2 per cent) is present, but this high acid content can never be obtained by oxidation of ordinary sulphite liquors as these contain a maximum of 0·1 per cent free SO_2, and not all combined SO_2 can be oxidized.

The formation of ozone can not increase the amount of sulphuric acid as this, in the first place, depends upon the available SO_2 in the liquor. In cases where the liquor has previously been used for the manufacture of spirit no free SO_2 is present, and it will in any case be necessary to add a small amount of sulphuric acid.

Papir. J. vol. 5 (1917) p. 14.

Pulp Paper Mag. Can. vol. 15 (1917) p. 343. See also vol. 15 (1917) pp. 88, 101, 140.

FUEL BRIQUETTES FROM SULPHITE LYE.

A Norwegian-Swedish company formed with capital of $426,667 to purchase and use Strehlenert's patent for fuel briquettes.

Pulp Paper Mag. Can. vol. 12 (1914) p. 97.

STREHLENERT'S PROCESS OF EXTRACTING FUEL FROM WASTE SULPHITE LIQUOR.

General description of the process, estimation of cost of production, and yield.

Translation from Papier-Ztg.
Paper Trade J. vol. 45 (1917) No. 7, p. 36.
Paper Makers' Mon. J. vol. 55 (1917) p. 284.
Pulp Paper Mag. Can. vol. 15 (1917) p. 1073.

STREHLENERT'S SULPHITE-FUEL PROCESS IN SCANDINAVIAN MILLS.

In addition to plant at Greaaker, Norway, for manufacture of fuel from waste sulphite liquor, according to Strehlenert's process, two Swedish companies are also installing the process in their mills.

Several Swedish mills intend to install the process but the machinery cannot be delivered at present.

Svensk Pap. Tid. (1917).
Pulp Paper Mag. Can. vol. 15 (1917) p. 343.
J. Ind. Eng. Chem. vol. 8 (1916) p. 1070.

Strehlenert, R. W.—PROCESS FOR EFFECTING A CHEMICAL DECOMPOSITION OF WASTE SULPHITE LIQUOR.

The liquor is heated indirectly by steam coils to a temperature at which the decomposition products are not appreciably precipitated on the highly heated coils. The final heating is effected by direct steam.

Norwegian Patent 27637 (1917).
Pulp Paper Mag. Can. vol. 15 (1917) p. 789.

Reilley, A. E. J.(United States Vice Consul at Stockholm)—UTILIZATION OF SULPHITE LYE IN SWEDEN.

At the laboratory of the Reymerholm Company (Reymerholms Gamla Spritforadlings A.B.) experiments have recently been completed with a new method for the utilization of refuse lye in the manufacture of sulphite. The difficulty in using the lye has consisted in concentrating it. By the new method the water is removed by freezing, which eliminates four-fifths of the water. The method is cheaper than that formerly employed and is considered to involve a reduction of the expenses by about 40 per cent. While the older method is based on the use of steam, water-power is used for the new. By this method, also, the organic substances in the lye are obtained in such a form that they can be used in many ways for dyestuffs, agglutinative substances, etc.

United States Commerce Reports, No. 281 (1917) p. 843.
Pulp Paper Mag. Can. vol. 15 (1917) p. 1220.

Strehlenert, R. W.—FUEL FROM WASTE SULPHITE LIQUOR.

The author reports on a number of improvements in the process of precipitating organic substances in waste sulphite liquor. Discussion of the chemical reactions that take place, heat requirements, and cost data.

Svensk Pap. Tid. vol. 20 (1917) No. 11 p. 128; No. 12, p. 144; No. 13, p. 158.

CARBONIZATION PROCESS FOR SULPHITE WASTE.

Waste liquor is evaporated to dryness and powdered to give 98 per cent through a 200-mesh screen. This fine material is burnt similarly to powdered coal. The fuel feed varied from 0·78 to 1 lb. per minute. Gas samples drawn from combustion chamber and along flame passages showed a furnace temperature of approximately 2,100 degrees. Tests were carried out at the demonstration plant of the Powdered-Coal Engineering and Equipment Company.

Paper vol. 21 (1917) No. 15 p. 18.

FODDER

Frank, A.—IMPROVEMENT RELATING TO THE SPENT LYES OF THE SULPHITE PROCESS.

Treatment of Waste Sulphite Liquor in order to recover sulphurous acid, preparing fodder and manure.

English Patent 13286 (1886).
J. Soc. Chem. Ind. vol. 6 (1887) p. 735.
(See " Sulphur " p. 154.)

Frank, A.—FODDER AND FERTILIZER FROM WASTE SULPHITE LIQUOR.

Austrian Patent 646 (1887).

POLLUTION OF RIVERS BY WASTE SULPHITE LIQUOR.

Belohoubek's process of manufacturing waste sulphite liquor into pulp molasses. The waste liquor is boiled after the addition of sulphuric acid, and neutralized with milk of lime, and when the lime sludge is removed the liquor is evaporated.

Papier-Ztg. vol. 15 (1890) p. 1282.

Mitscherlich, A.—PROCESS AND APPARATUS FOR UTILIZATION OF WASTE SULPHITE LIQUOR.

Covers previous German patents.

Austrian Privilegium 112 (1894).
(See " Gums, Adhesives, and Sizing Materials " p. 68.)

Goldschmidt, E.—PROCESS FOR PRECIPITATING ORGANIC MATTERS FROM THE WASTE SULPHITE LIQUOR.

Treatment of the organic substances with benzolchloride by the Schotten-Baumann method for the preparation of fodder. One part benzoylchloride in slightly alkaline solution to 100 parts liquor.

German Patent 97,935 (1897).
Chem. Zentr. (1898) part II p. 616.
Papier-Ztg. vol. 23 (1898) p. 2664.

Detsinyi, F.—SULPHITE LIQUOR FOR DENATURING CATTLE SALT.

Briquetting of waste liquor mixed with common salt.

Austrian Patent 10987 (1898).
Papier-Ztg. vol. 23 (1898) part I p. 950.

Lehmann, E.—PROCESS FOR PRODUCING EASILY DIGESTIBLE FODDER-STUFF FROM STRAW, WOOD, ETC.

The products are heated with waste sulphite liquor.

German Patent 128661 (1900).

Frank, A.—SULPHITE LIQUOR AS A CATTLE FOOD.

The author thinks that further investigations should be made into this subject.

Papier-Ztg. vol. 29 (1904) part II p. 2465.

Frank, A. and Lehmann, E.—WASTE SULPHITE LIQUOR AS CATTLE FOOD.

Discussion of the possibilities for waste sulphite liquor as cattle food.

Papier-Ztg. vol. 29 (1904) part II p. 3368.
Wochbl. Papierfabr. vol. 35 (1904) p. 3338.

Knoesel, Th.—WASTE SULPHITE LIQUOR AND FODDER SCARCITY.

Use of waste sulphite for fodder.

Papier-Fabr. vol. 2 (1904) p. 759.

Frank, A.—REPORT ON FEEDING WITH WASTE SULPHITE LIQUOR.

Papier-Ztg. vol. 31 (1906) part II p. 3322.

Lehmann, E.—COOKING OF WOOD SUBSTANCES FOR THE PRODUCTION OF CATTLE FOOD.

German Patent 169880 (1905).
Papier-Ztg. vol. 31 (1906) part II p. 2548.

Medicus and Engler.—UPON FRANK'S PROCESS FOR PURIFICATION OF WASTE LIQUOR AND RECOVERY PROCESS.

Schubert, Zellstoffabrikation (1906) p. 253.

Stutzer, A.—PROCESS FOR PREPARING A FOODSTUFF FROM WASTE SULPHITE LIQUOR.

After removal of the sulphurous acid the tar-like, unpleasant-tasting, decomposition products of resinous matters and bitter substances are removed by means of a suitable oil. The sulphurous acid is removed by addition of aldehyde, forming formaldehyde, sulphurous acid and its calcium compound.

German Patent 215273 (1908).
Papier-Ztg. vol. 34 (1909) part II p. 3758.
Chem. Zentr. (1909) part II p. 1783.

Stutzer, A.—RESEARCHES ON SULPHITE LIQUOR AS A FEEDING STUFF.

The waste liquors from the manufacture of sulphite wood-pulp contain on an average 120 grammes of organic matter and 10-15 grammes of mineral matter per litre (1.2 lb. organic matter and 0.1-0.15 lb. mineral matter per gallon). The calorific value of the dry substance, including the mineral matter, is 4,250 calories per kilogramme; the organic matter has a greater calorific value than starch or cellulose. The author has therefore been led to investigate the possibility of utilizing the large quantities of waste liquors, which now pollute the rivers, for the purpose of feeding cattle. The most deleterious constituent of the liquors in this respect is the sulphurous acid, both free and in the form of salts, that combined with the organic matter being probably harmless. It is impossible to remove the sulphur dioxide by precipitation in the form of calcium monosulphite; chalk apparently has no effect in this direction and lime removes only a portion of the sulphurous acid. In the case of lime and the fixed alkalies an abnormally large proportion is required to neutralize the liquors owing to their action on the carbohydrates in forming acid bodies, presumably saccharides; ammonia has no such action. In order to render the liquors suitable for feeding purposes the proportion of sulphurous acid must be reduced below 0.1 per cent. The only way in which the author has been able to effect this satisfactorily is by combination with an aldehyde, e.g. formaldehyde. If the liquors be concentrated to one-half or one-third of their bulk a portion of the sulphurous acid is expelled as gas. Before the sulphurous acid can combine with the formaldehyde it must be converted into calcium bisulphite. This is best done by the addition of a small excess of calcium carbonate; the liquid still has an acid reaction, owing to the organic matter, and calcium monosulphite is not produced. The removal of the sulphurous acid is more complete the larger the quantity of formaldehyde added. A sample of liquor containing 2.3 grammes of sulphur dioxide per litre, when treated with 2.5 c.c. of formalin per litre, showed only 0·809 grammes; with 5 c.c. per litre this was reduced to 0.369 gramme, and with 20 c.c. to 0.016 gramme. It is difficult to control the process analytically because a portion of the sulphur dioxide found on distillation with dilute phosphoric acid must be derived from the hydrolysis of harmless organic compounds.

In fact, the hydroxymenthane-sulphonic acid itself, formed by the addition of formaldehyde, is not stable, though more so than the organic sulphonic acids of the liquors. Before the liquors can be used the excess of formaldehyde must be fixed in a harmless form. This may be done by neutralizing the liquid with ammonia; in practice the author makes use of the nitrogenous matters of molasses. Experiments have been made upon sheep with a fodder prepared as follows: 100 litres (22 gallons) of waste sulphite liquor, evaporated to half the volume, treated with powdered limestone and formalin, filtered, further evaporated, then mixed with 20 kilogrammes (44 lb.) of best molasses and finally with 5.25 kilogrammes (11.5 lb.) of finely chopped peat-moss. About 20 litres (4·4 gallons) of liquor were allowed per 1,000 kilogrammes (2,204 lb.) of body weight of the animal.

Z. angew. Chem. vol. 22 (1909) p. 1999.
J. Soc. Chem. Ind. vol. 28 (1909) p. 1162.
Papier-Ztg. vol. 34 (1909) part II pp. 3210, 3251.
Wochbl. Papierfabr. vol. 40 (1909) p. 3640.
Chem. Abs. vol. 4 (1910) p. 107.

Stutzer, A.—CATTLE FOOD FROM SULPHITE LIQUOR.

The main object of the process is to remove sulphurous acid from the liquors, and for this purpose the latter are treated with formaldehyde, about 0·5 kilogrammes (1·1 lb.) of 40 per cent formaldehyde solution being added to every 100 litres (22 gallons) of the sulphite liquor. The mixture is then neutralized by the addition of calcium carbonate and concentrated. The excess of formaldehyde added is partly carried away by the carbon dioxide evolved during the neutralization, and the remainder may be eliminated by the addition of small quantities of ammonia or of substances, such as molasses, containing ammonium salts.

French Patent 402871 (1909).
J. Soc. Chem. Ind. vol. 28 (1909) p. 1323.

Vogel, J. H.—WASTE SULPHITE LIQUOR AS FODDER.

Discussion of Stutzer's process (German Patent 215273) at the annual meeting of the Association of German Pulp and Paper Chemists (1908).

Papier-Ztg. vol. 34 (1909) part I p. 3.
Z. angew. Chem. vol. 23 (1910) p. 116.
Chem. Ztg. vol. 33 (1909) p. 1187.

Stutzer, A.—SULPHITE PULP WASTE AS FODDER.

Continuing his investigations on the use of the waste lyes from sulphite wood-pulp mills as fodder for cattle, the author remarks that the sulphurous acid must be eliminated and that his formaldehyde process (J. Soc. Chem. Ind., vol. 28 (1909), p. 1162) has proved in practice to be too costly. Substances which increase the ash of the product are also out of the question. The most satisfactory neutralizing agent is ammonia, which converts the calcium bisulphite into the insoluble monosulphite and if used in slight excess liberates some of the sulphurous acid which is in combination with the aldehydes; the lignosulphonic acids are not decomposed. The ammonium sulphite produced is dissociated on heating, and ammonia and sulphur dioxide are volatilized during the evaporation of the lyes. Calcium salts are also precipitated if ammonium carbonate be employed. It has been stated by Kellner that ammonia in combination with organic acids can be assimilated by animals. Further, the bitter substances are so changed during the treatment that in conjunction with beet molasses the products are readily eaten by cattle. Suitable proportions are, 1 part molasses, 4 parts of the prepared wood extract, and 5 parts of sliced potatoes. The product has not been tried on a large scale but experimental results have been satisfactory. The ammonia from coke ovens is too costly for the purpose, and the author recommends the use of calcium nitride. Experiments have also been made with satisfactory results on the use of the evaporated waste lyes in finishing textiles. For this purpose the colouring matters are the first removed from the lyes.

Chem. Ztg. vol. 34 (1910) p. 1352.
J. Soc. Chem. Ind. vol. 30 (1911) p. 18.
Chem. Abs. vol. 5 (1911) p. 2946.

Muller, M.—SULPHITE LYES FOR USE AS CATTLE FOOD.

The waste lye, after treatment with sodium sulphate and separation of the precipitated calcium sulphate, is passed into the last element of a multiple-effect evaporator in the known manner, the liquor ascending externally heated tubes, in the form of a thin film, on the inner surface. The lye in this way is freed from sulphurous acid which is carried away by steam. The mixture of steam and sulphurous acid is conducted over lime, which absorbs the acid, on its way to the condenser. The further evaporation of the lye, after expulsion of the sulphurous acid, is effected in any suitable manner.

German Patent 241282 (1910).
Chem. Abs. vol. 6 (1912) p. 2170.
J. Soc. Chem. Ind. vol. 31 (1912) p. 123.

Frank, A.—CATTLE FOOD FROM WASTE SULPHITE LIQUOR.

The digestibility of the wood extract in the waste liquor is not yet determined. It will be difficult to secure the required quantity of molasses and dry potatoes which it is proposed to add to the prepared fodder liquor, and this might effect the economy of the process.

Report of the annual meeting of Pulp and Paper Chemists, Berlin, Germany (1910) p. 67.

La Société Anonyme Anciens Établissements L. De Naeyer.—PROCESS FOR UTILIZATION OF WASTE SULPHITE LIQUORS.

The sulphurous acid combined with inorganic or organic substances is decomposed by the action of sulphuric or phosphoric acid. One modification of the process is to concentrate and neutralize the liquor and to ferment it for the production of alcohol. The remaining liquor can be further concentrated for use as binding material or forage.

Belgian Patent 255551 (1903)

Stutzer, A.—UTILIZATION OF WASTE LIQUORS FOR FORAGE.

When the bitter substances were made appetizing by the addition of molasses the appetite of the animals experimented with increased. Fodder for spreading could be made by addition of bran and even peat-meal. Also, sawdust can be used. Bran and potato flakes are better. When the calcium salts have been removed favourable results were obtained with sheep. The process of purification should be further improved and the efficiency should be tested.

Report on the annual meeting of German Pulp and Paper Chemists (1910) p. 44.

Stutzer, A.—FORAGE WITH WASTE LIQUOR PRODUCTS.

The author succeeded in removing the bitter substances and eliminating the aperient effect. However, the tanning substances make the fodder difficult to digest.

Report on the annual meeting of German Pulp and Paper Chemists (1912) p. 31.

Konig, J.—THE SO-CALLED NITROGEN-FREE EXTRACTIVES IN FOODSTUFFS.

Paper dealing with the above. The author divides the above into pentosans, hexosans, lignin, and cutins.

Z. Nahr. Genussm. vol. 26 (1913) p. 273.
Chem. Zentr. (1913) part II p. 1700.

Konig, J.—CELLULOSE, FODDER, ETC.

Swedish Patent 40438 (1916).
Chem. Abs. vol. 10 (1916) p. 2045.

Konig, J.—MANUFACTURE OF FODDER FROM WASTE SULPHITE LYES.

Waste sulphite lye is mixed with the residual liquid obtained in the treatment of wood with dilute alkalies and acids with the aid of heat and pressure (see German Patent 265483), and the mixture is evaporated, neutralized, and freed from sulphurous acid. The product can be used as a cattle food. The sulphite lyes may be submitted to a preliminary treatment with acid or alkali, which enables them, after neutralizations and separation of sulphurous acid, to be evaporated separately; this product also can be used as a food by itself. The residual liquid obtained from the acid and alkali treatment of cellulose may be treated for the extraction of resins, tannins, sugars, etc., before being mixed with the sulphite liquor.

French Patent 469768 (1914).
United States Patent 1128154 (1915).
J. Soc. Chem. Ind. vol. 34 (1915) pp. 47, 299.
Paper vol. 15 (1914) No. 22 p. 17.

Goy, S.—INVESTIGATIONS ON THE DIGESTIBILITY OF WASTE SULPHITE LIQUORS.

The liquor itself is digestible, but the experiments were not successful.

Z. angew. Chem. vol. 26 (1913) Rep. No. 82 p. 602.
Landw. Vers. St. vol. 82 (1913) p. 1-92.
Chem. Abs. vol. 7 (1913) p. 4023.

Konig, J.—PROCESS FOR MANUFACTURE OF A FODDER FROM WASTE SULPHITE LIQUOR.

Konig's cooking process.

Norwegian Patent 26029 (1915).
Papir J. vol. 3 (1915) No. 15 p. 203.

E. Trainer's Heirs.—UTILIZATION OF SULPHITE-CELLULOSE BACK WATERS.

German Patent 283931 (1911).
(See " Fertilizer " p. 141.)

Konig, J.—RENDERING WASTE SULPHITE LIQUOR HARMLESS, AND UTILIZING IT.

The liquor is heated for a few hours with indirect steam and made slightly alkaline with milk of lime or limestone. After the liquor is cooled down and the precipitate has settled, the clear solution is aerated by allowing it to trickle over galvanized-wire gauze and is again neutralized by passing over limestone. The dark-brown liquor is concentrated by indirect heating and the thin syrup is mixed with various feeding materials. The mixtures remain permanent if the water content is brought down to about 12 per cent. The ash content is about 10 per cent, SO_2 combined with lime 0·1-0·4 per cent, and organically combined sulphur 1-2 per cent.

Z. Nahr. und. Genussm. vol. 31 (1916) p. 171.
Papir J. vol. 4 (1916) No. 16 p. 187.
Z. angew. Chem. vol. 29 (1916) Rep. p. 379.
Chem. Abs. vol. 10 (1916) p. 3114.
J. Soc. Chem. Ind. vol. 35 (1916) p. 960.

Konig, J.—FODDER AND CELLULOSE FROM WOOD.

The wood is subjected to a pre-treatment with dilute mineral acids (H_2SO_4 or HCl) and dilute alkalies (preferably NH_4OH) or with one of these solutions alone under varying pressure. The materials are then treated further according to the usual sulphite process. The liquors are after complete neutralization evaporated alone or together and worked up to fodder. The first liquor, rich in sugar, may be worked up separately for alcohol or other product and the residual liquor treated with the sulphite liquor for use as fodder.

German Patent 284715 (1914).
Chem. Abs. vol. 10 (1916) p. 76.

FERTILIZER

Tilghman, B. C.—UTILIZATION OF WASTE SULPHITE LIQUOR FOR FERTILIZING PURPOSES.

Gumming properties of the concentrated liquor.

English Patent 2924 (1866).
United States Patent 70485 (1867) 92220 (1869).
E. Kirchner, Holzzellstoffabrikation 1907 p. 14.

Frank, A.—IMPROVEMENTS RELATING TO THE SPENT LYES OF THE SULPHITE PROCESS.

English Patent 13286 (1886).
Austrian Patent 646 (1887).
(See " Sulphur " p. 154.)

Frank, A.—PREPARATION AND RECOVERY OF SULPHUROUS ACID IN THE SULPHITE PROCESS.

Irrigation of meadows with the purified waste liquor.

(See " Sulphur " p. 154.)

Brookes, A. G. (from Trippe, W.)—TREATMENT AND UTILIZATION OF WASTE SULPHITE LIQUOR.

English Patent 8088 (1901).
See " Gums, Adhesives, and Sizing Materials " p. 68.)

Arlt, O.—FERTILIZER FROM SULPHITE LIQUOR AND THOMAS' SLAG-MEAL.

Sulphite liquor of 25° Bé. is mixed with an equal quantity of Thomas' slag-meal. The citrate solubility of the phosphate is thereby greatly increased.

German Patent 128213 (1898).
Chem. Zentr. (1902) part I p. 446.
Chem.-Ztg. vol. 26 (1901) p. 229.
Papier-Fabr. vol. 3 (1905) p. 785.
Schubert. Zellstoffabr. (1906) p. 270.

Knoesel, Th.—UTILIZATION OF WASTE SULPHITE LIQUOR AS MANURES.

The spent liquors from the manufacture of sulphite cellulose have frequently been used, after treatment, for manurial purposes, but they are difficult to transport and the soil is capable of assimilating only a limited quantity.

In order to convert them into dry and not too readily soluble manure, the author concentrates them to about 25° Bé., and then mixes them with an approximately equal weight of Thomas' slag-meal. There is a spontaneous evolution of heat, and in a short time a solid mass, equally distributed, is obtained. The products thus obtained are brownish-yellow in colour, have a pleasant odour, recalling vanillin, and only dissolve slowly in water, yielding a brownish-yellow solution.

The chemical composition differs greatly from that of Thomas' meal, which only contains about 75 per cent of its phosphoric acid in a citrate-soluble form whereas in the new manures practically the whole of the phosphoric acid is soluble.

The following analyses show the amount of potassium oxide and phosphoric acid in four of these preparations. In the case of the fourth sample a considerable excess of slag-meal had been added, so that less phosphoric acid was in the citrate-soluble form.

	I Per cent	II Per cent	III Per cent	IV Per cent
Total phosphoric acid (P_2O_5)	8·61	8·68	8·85	10·60
Citrate-soluble acid (P_2O_5)	8·45	8·45	8·40	9·10
Potassium oxide (K_2O)	0·30	0·30	0·22	0·29

The alkali in the Thomas' meal is neutralized by the sulphurous and ligninsulphonic acids in the sulphite liquors, so that the new manures can be used, even in admixture, with ammoniacal manures without fear of injuring the plants. Owing to the presence of the organic matter, the addition of peat usually made to Thomas' meal is unnecessary in the case of the new products. The process here described is protected by German Patent 128213.

D. Landw. Presse (1902) No. 4.
Chem.-Ztg. vol. 26 (1902) p. 229.
Chem. Zentr. (1902) part I p. 955
Papier-Ztg. vol. 28 (1903) part I p. 288.
J. Soc. Chem. Ind. vol. 21 (1902) p. 489.

Stutzer, A.—UTILITY OF KNOESEL MEAL.

Stutzer doubts the usefulness of the Knoesel meal.
D. Landw. Presse (1902) No. 63.

AN ARTIFICIAL FERTILIZER.

A process has been recently patented for preparing a useful fertilizer in a dry condition from waste sulphite-cellulose liquors. These are evaporated to a syrupy consistency and mixed with an equal quantity of Thomas' meal. The mixture almost immediately becomes solid and can be broken into small pieces. Nearly the whole of the phosphoric acid of this fertilizer is soluble in citrate solution, i.e. is in a condition suitable for utilization as a fertilizer; in fact, 98 per cent of the phosphoric acid is citrate-soluble as against 83 per cent in the original Thomas' meal.

Papier-Ztg. vol. 27 (1902) p. 1508.
J. Soc. Chem. Ind. vol. 21 (1902) p. 783.

Hoffmann, M.—SULPHITE LIQUOR AS A FERTILIZER.

The author considers Knoesel's patent (German Patent 128213) of little value.
Bodenpflege und Pflanzenbau (1904) p. 320.

Ahrens, F. B.—UTILIZATION OF SULPHITE LIQUOR AS MANURE.

The author has examined the method proposed by Knoesel (J. Soc. Chem. Ind. vol. 21 (1908) p. 489) for the utilization of waste sulphite-cellulose lyes. The lye was concentrated to about 25° Bé. and mixed with an equal weight of Thomas' slag-meal. In no case was a rise of temperature of more than a few degrees observed, nor was the citrate solubility of the phosphoric acid increased. The organic constituents of the lyes are in no way changed by the treatment with the Thomas' slag-meal, except that a small proportion combines with the lime and is thereby rendered insoluble, and the method cannot therefore be considered of much value.

Papier-Ztg. vol. 30 (1905) part I p. 1539.
Chem. Zentr. (1905) part I p. 700.
Chem.-Ztg. vol. 4 (1905) p. 40.
J. Soc. Chem. Ind. vol. 24 (1905) p. 343.

Knoesel, Th.—UTILIZATION OF WASTE SULPHITE LIQUOR.

Use of Thomas' meal for sulphite liquor manure. Experiments.
Papier-Fabr. vol. 3 (1905) p. 1914.

KNOESEL MEAL.

See German Patent 128213 (1898) Arlt and Knoesel.
D. Landw. Presse (1902) Nos. 4 and 63; (1905) Nos. 4 and 13.
Chem.-Ztg. vol. 26 (1902) p 329, vol. 27 p. 21, vol. 28 p. 38.
Chem. Zentr. (1902) part I p. 955.
Papier-Ztg. vol. 28 (1903) part I p. 288. vol. 30 (1905) part I p. 1539, vol. 29 (1904) part II p. 3367.
Wochbl. Papierfabr. vol. 33 (1905).
Bodenpflege und Pflanzenbau, Berlin (1904) p. 320.
Papier-Fabr. vol. 2 (1904) p. 759; vol. 3 (1905) p. 1714.
Chem-Zeitschr. (1905) No. 4 p. 40.
Z. angew. Chem. vol. 17 (1904) No. 47.
Schubert, die Zellulosefabrikation (1906) p. 270.

Knoesel, Th.—UTILIZATION OF WASTE SULPHITE LIQUOR.

Knoesel meal. Discussion of remarks made by Klein and Ahrens.

Wochbl. Papierfabr. vol. 38 (1908) part II p. 2542.
Report. Techn. Journ. Lit. (1907) p. 309.

Knoesel, Th.—MANURE AND ITS PROCESS OF MANUFACTURE.

Calcium cyanamide is intimately mixed with sulphite liquors (from the manufacture of cellulose) which may or may not have been neutralized, say by the addition of calcium carbonate. For example, 60 kilogrammes (132 lb.) of calcium cyanamide are intimately mixed with 150 litres (33 gallons) of sulphite liquor of 14·5°Bé., and then 100 litres (22 gallons) of liquor of 38·5° Bé., are added little by little, with continued stirring; after further stirring and allowing to stand the mass acquires such consistency that it may be ground, and 400 kilogrammes (880 lb.) of dry manure are obtainable, the product, owing probably to the organic matter and potassium derived from the liquor, being superior to calcium cyanamide and more rapid in its action. Or, 65 kilogrammes (143 lb.) of calcium cyanamide are mixed with 1,000 kilogrammes (2,204 lb.) of ordinary non-concentrated sulphite liquor, (6·5°Bé.) and the mass is heated, after which the mixture is left to stand for some time until precipitation is complete, and the liquor is then separated and the precipitate washed, or the whole is employed as a manure without separating. The precipitate contains 81·55 per cent of the organic matter present in the sulphite liquor.

French Patent 423562 (1910).
J. Soc. Chem. Ind. vol. 30 (1911) p. 638.

Stutzer, A.—USE OF SULPHITE LYES ON SEWAGE FIELDS.

Near the city of Konigsberg are two sulphite wood-pulp mills, one above and the other below the city. In 1910 the former received permission, on certain conditions, to discharge its waste lyes into the town sewers. The chief conditions were, acidity not to exceed 0·6 grammes per litre, temperature not to exceed 40°C., and the flow to be regulated to a constant average. These conditions were framed from the point of view of minimizing the corrosion of iron pipes, etc. Little regard was paid to the fact that the sewage waters were partially utilized some miles away for the irrigation of the fields, although at times the greater portion found its way direct to the sea. During the year 1910 much trouble was experienced as the result of the inclusion of the sulphite lyes in the town drainage. In the town, rain-water pipes, etc., were corroded by the fumes of the sulphur dioxide rising from the drains, and in the sewage fields the rye crops were severely injured. Investigation showed that the degree of acidity permitted was far too high, and although the discharge of lye from the mill was regular the quantity of town sewage was so variable that at certain times, especially in the early morning, the dilution of the lye was insufficient. Vegetation is far more susceptible to the action of acid than are iron pipes, in fact the noxious effect of waste sulphite lyes on vegetation is probably entirely due to their acidity. In the year 1911, under the author's advice, the pulp-mill undertook to increase the proportion of lime added to the waste lyes, so that their acidity, calculated as sulphuric acid, was reduced to 0·2 gramme per litre; further, the discharge from the mill was conducted for a long distance around the outside of the town before joining the main sewer, and in its course received a very much larger quantity of surface drainage water than before. These alterations were entirely successful; at the sewage fields the acidity never exceeded 0·06 gramme per litre and sometimes the sewage was even slightly alkaline; the proportion of sulphite lyes present was also reduced to a maximum of 23 parts per 1,000, as compared with over 100 parts per 1,000 previously. Not only was the rye unharmed by the presence of the lyes but a beneficial effect was apparently produced owing to the organic matter thus introduced into the sewage.

Papier-Ztg. vol. 36 (1911) pp. 2015, 2093, vol. 35 (1910) p. 104.
Wochbl. Papierfabr. vol. 42 (1911) p. 2685.
J. Soc. Chem. Ind. vol. 30 (1911) p. 976.
Chem. Abs. vol. 5 (1911) p. 3622.

Hoesch & Co.—PREPARATION OF FERTILIZER FROM WASTE SULPHITE LIQUOR.

Belgian Patent 239604.
Hungarian Patent Application 4348 (1911).

Knoesel, Th.—USE OF WASTE SULPHITE LIQUOR FOR IRRIGATION.

It is reported that irrigation with sulphite liquor produces bad odours. However, according to Stutzer such irrigation has given favourable results.

Papier-Ztg. vol. 36 (1911) p. 2193.

WASTE SULPHITE LIQUOR AS A FERTILIZER.

Experiments by M. Boulanger have determined that sulphur (in the form of the familiar "flowers of sulphur") is a valuable fertilizer of soil. Its action is not direct however as in the case of other mineral fertilizers; it acts as a modifier of the bacterial flora contained in ordinary soil; it acts as a destroyer of noxious microbes on the one hand while on the other it is favourable to the useful bacteria flora. When the soil has been sterilized by heat the sulphur becomes inoperative.

Paper vol. 8 (1912) No. 10 p. 18.

Knoesel, Th.—WASTE SULPHITE LIQUOR AS A MANURE.

Report on favourable results with waste liquor products of various kinds as a manure.

Holzstoff-Ztg. vol. 20 (1913) p. 775.

Knoesel, Th.—A NEW FERTILIZER WITH LARGE AMOUNTS OF SLOWLY SOLUBLE ORGANIC SUBSTANCES.

Description of preparation, composition and effect of fertilizer from calcium cyanamide and waste liquor.

Z. Sauerstoff Stickstoff Ind. vol. 4 (1912) p. 65.

Muller, M.—PROCESS FOR TRANSFORMING CALCIUM CYANAMIDE INTO A NON-DUSTING AND SLIGHTLY CORRODING MASS BY USE OF WASTE SULPHITE LIQUOR.

The residue obtained by evaporation of the liquor (containing 12 per cent water) is mixed with raw calcium cyanamide or the powdered liquor residue, with a lower water content than required, is mixed with the cyanamide and the hygroscopic mixture allowed to absorb as much water as necessary to produce a non-dusting and carbide-free material of favourable fertilizing effect.

German Patent 262473 (1912).

Chemische Fabrik Floersheim.—MEANS OF IMPROVING THE SOIL.

The liquor is heated in a current of air or oxygen to the desired consistency. To this product may be added other substances, acting as nutriment, fertilizer, etc.

German Patent 247119 (1910).

Nitsche, P.—THE SOURCES OF NITROGEN IN AGRICULTURE AND THE UTILIZATION OF WASTE SULPHITE LIQUOR.

When free sulphurous acid and sulphuric acid is removed from the liquor, which is made slighty alkaline with lime, it is claimed that it forms a good medium for the culture of nitrogen-binding bacteria.

Woch. J. angew. Chem. vol. 43 (1912) p. 4045.
Z. angew. Chem. vol. 25 (1912) p. 2058.
Chem. Abs. vol. 7 (1913) p. 528.
J. Soc. Chem. Ind. vol. 21 (1912) p. 1000.

Hoesch & Co.—FERTILIZER FROM SULPHITE LIQUOR.

Waste sulphite liquors are treated directly, or after concentrating or evaporating to dryness, with nitrogen-fixing bacteria, the material forming an advantageous medium for the culture of the bacteria, and the product is applied to the soil as a fertilizer. Or, the liquor, after preliminary treatment such as neutralizing, drying, and grinding, is applied directly to the soil, to be acted upon by the nitrogen-fixing bacteria naturally present.

French Patent 434943 (1911).
English Patent 21994 (1911) (to P. A. Newton).
J. Soc. Chem. Ind. vol. 31 (1912) pp. 351, 696.

Stutzer, A.—FERTILIZER FROM SULPHITE LYES.

Sulphite-cellulose waste lyes, to which fertilizers may be added, are absorbed by peat moss litter, and the mixture is heated to about 120° C. in a suitable drying apparatus, e.g. of the rotary-drum type, provided with an acid-resisting lining. It is stated that the dried moss can be reduced to a powder.

J. Soc. Chem. Ind. vol. 32 (1913) p. 1165.

Siebner, E. O.—THE CALCIUM CYANAMIDE INDUSTRY.

Chem.-Ztg. vol. 37 (1913) p. 1057.

Stutzer, A.—PROCESS FOR PREPARATION OF A MANURE FROM WASTE SULPHITE LIQUOR.

The liquor is absorbed by peat and the product heated under continuous aeration to a temperature a little above 100° C. in order to destroy compounds injurious to the plants and to transform the peat into a crumbling mass, which is easily decomposed by the bacteria of the soil.

German Patent Application St. 17127 (1912).

Stutzer, A.—WASTE SULPHITE LIQUOR IN RELATION TO AGRICULTURE.

Fertilizing tests with the dry residue of the liquor gave increased yield. The liquor should not be used with large amounts of nitrogen, as in this case a decrease in yield may take place. Further laboratory tests showed that the organic substance in the liquor has a good fertilizing effect in clay soil deficient in humus and seems to improve soils poor in humus and nitrogen.

Wochbl. Papierfabr. vol. 42 (1913) p. 2685.
Landw. Ztg. vol. 62 (1913) p. 139.
Chem. Abs. vol. 7 (1913) p. 4037.
Pulp Paper Mag. Can. vol. 11 (1913) p. 769.
Paper, vol. 11 (1913) No. 8, p. 22.

Stutzer, A.—MANURING TESTS WITH CELL-PITCH POWDER.

Tests on the field with finely powered cell-pitch (5,000 kilogrammes on 1 hectare) (4,460 pounds per acre) gave unfavourable results with potatoes on good soil.

Muller, Literatur der sulfitablauge (1913) p. 12.

Thalan, W.—THE EFFECT OF SULPHITES ON PLANTS.

Calcium sulphite has not caused any decrease in yield on clay and sandy soil but seems to affect peat soil unfavourably. In water growths an increased addition of calcium sulphite has caused a decrease in growth.

Edited by F. Stollberg, Merseburg 1913.

Kern, L.—FERTILIZER FROM SULPHITE-CELLULOSE WASTE LYE.

The waste lyes are mixed with kieselguhr (infusorial earth), containing mineral and organic substances, such as is found, for example, in Algeria, Bohemia, and Virginia. By the combination, in this way, of two practically worthless products, a fertilizer is obtained which is suitable for peaty soils poor in silica and for plants rich in silica, e.g. maize, cereals, grass, etc.

German Patent 278492 (1914).
Papier-Ztg. vol. 39 (1914) p. 2500.
J. Soc. Chem. Ind. vol. 34 (1915) p. 240.

Lassar-Cohn.—DISPOSAL OF SULPHITE WASTE LYES.

A report on the disposal of the waste lyes from two sulphite-mills (pulp) in the neighbourhood of Konigsberg. The effluent from one mill is discharged into the town sewers for irrigating the sewage fields. The admixture of the sulphite lyes with the sewage has produced a beneficial effect upon the crops, the large proportion of non-nitrogenous organic matter introduced by the lyes having an effect similar to that produced by the straw of farmyard manure when used in conjunction with town-sewage, great bacterial activity being thereby induced. The soluble sulphur compounds probably also play an important part, for it has been shown that electrolytically prepared phosphates are by no means so successful as ordinary superphosphates, owing to the absence of calcium sulphate. The waste lyes from the other mill, situated at the mouth of the river, are carried out into the bay by tank steamers and gradually discharged on the voyage. Here again, a beneficial result is recorded. The organic matters of the lye encourage the growth of plankton, which attracts the fish, and the local fishery statistics show considerable increase. The question of profitable or even costless disposal of the lyes still awaits solution. The hydroscopic nature of the solid matters of the lyes makes them unsuitable for fuel briquettes, although small quantities are successfully applied for briquetting blast-furnace dust; the evaporation, however, is a difficult problem. Over 2 million kilogrammes (2,204 short tons) of waste lyes are produced daily by the German pulp-mills alone.

Chem.-Ztg. vol. 38 (1914) p. 657.
J. Soc. Chem. Ind. vol. 33 (1914) p. 639.

Kern, L.—TESTS WITH FERTILIZER FROM INFUSORIAL EARTH AND WASTE SULPHITE LIQUOR.

Report on favourable results with a mixture of waste sulphite liquor and impure infusorial earth (German Patent 278492, 1914) and on sandy or heathy soils. The waste liquor alone is not a fertilizer and the SO_2 content is injurious to the plant growth. Waste liquor in mixture with impure infusorial earth which contains soluble salts of silica and phosphoric acid and calcium carbonate has given good results. Frank mentions in a discussion that waste sulphite liquor alone when neutralized is also a good fertilizer for poor soil as it increases the humus content and also contains some potassium, phosphoric acid, and magnesia.

Wochbl. Papierfabr. vol. 46 (1915) p. 278.
Chem. Abs. vol. 9 (1915) p. 1086.

E. Trainer's Heirs.—UTILIZATION OF SULPHITE CELLULOSE BACK-WATERS.

The high content of SO_2 or of compounds splitting off SO_2 readily, and of lime and the almost entire absence of albuminous substances, have been prime factors in rendering the waste liquor inapplicable as fertilizers and fodder. The liquors make a good medium for oxidizing micro-organisms, by the action of which the sulphur compounds are oxidized to less injurious compounds. The organisms *B. subtil.*, *B. vulgarus*, *B. acet.*, *B. mycoid.*, *B. pasteur*, *B. acid lact.*, are suitable for this purpose. In addition to the oxidation the liquors are enriched by the organisms themselves in useful organic compounds. The organism selected is cultured on the soil containing the lyes in pure culture, and then the principal portion of the lye is inoculated with this pure culture. The conversion of the lye is favoured by aeration so that the lye is allowed to trickle over step-work or the like and heated to a definite temperature. In order to incorporate albuminous matter, the liquors, freed as much as possible from sulphur compounds, are fermented with yeast, and the mass is then dehydrated until fit for use as fodder or fertilizer. Wood waste can be rendered fermentable by suitable treatment and added to the liquors before fermentation. Also, fermentable matter from the sugar or starch industry can be used.

German Patent 283931 (1911).
Chem. Abs. vol. 9 (1915) p. 2591.

Kressel, E. C. L.—FERTILIZER FROM WASTE SULPHITE LIQUOR.

One thousand pounds of concentrated waste sulphite liquor (specific gravity, 1·208-1.330) is mixed with 50-100 pounds of stable manure and with about 50 pounds of distillers' or brewers' yeast, and the mixture is allowed to ferment for 24 hours at 30°-40° C. with or without the addition of a liquor obtained by leaching marsh soil. After the fermentation is well under way there is added another 1000 pounds of waste sulphite liquor at a temperature of 40°C, and while agitating there are also slowly added 150 pounds of CaO (60 mesh powder), 80 pounds of rock salt, and 400-1,000 pounds of feldspar or basic slag (or a mixture of them). The mass gradually thickens, becomes granular, and finally sets hard, and on pulverizing yields a brown non-hygroscopic powder useful as a fertilizer. If the fermentation is allowed to continue too long a less active product is obtained and the hardening of the product is retarded. NaCl, KCl, NH_4Cl, or alkaline earth metal chlorides may be used instead of feldspar or slag.

United States Patent 1225825 (1917).
Chem. Abs. vol. 11 (1917) p. 2255.
J. Soc. Chem. Ind. vol. 36 (1917) p. 730

DYE

Cross and Bevan.—IMPROVEMENT IN THE MANUFACTURE OF MORDANTING AND FINISHING MATERIAL FOR TEXTILE FABRICS, PAPER, ETC. (GELALIGNOSIN).

The specification of this invention describes the manufacture of substances which the authors call "gelalignosin" and "albulignosin". "When woods and many fibrous vegetable substances are boiled under pressure in a solution of" a sulphite, as in Ekman's and other processes, "a liquid is obtained holding in solution a large amount of organic matter." The authors have found that if this liquid be acidified and either gelatin or albumen be then added to it a peculiar substance which they have named "lignosin" is precipitated from it; in the one case in combination with the gelatin used, in the other case in combination with the albumen. It is the compounds so obtained which they have named respectively gelalignosin and albulignosin. They find that both these bodies "are suitable for use as size, as mordants, and as vehicles for colours and pigments."

English Patent 1548 (1883).
J. Soc. Chem. Ind. vol. 2 (1883) p. 541.

Ekman, C. D.—IMPROVEMENTS IN OBTAINING USEFUL PRODUCTS FROM THE LIQUORS RESULTING FROM THE MANUFACTURE OF CELLULOSE BY THE SULPHITE PROCESS.

The improvements relate to a method of recovering some of the organic compounds contained in the spent liquor from the manufacture of cellulose fibre from wood by the sulphite process. The waste liquor is first clarified by allowing it to settle or by passing through filter beds, after which it is concentrated, preferably to about 63° T.W. at 85°C., in suitable vessels having an acid-resisting lining, and heated by steam in a leaden coil or jacket. Before evaporating, the liquor may be made alkaline by the addition of any of the caustic or carbonate compounds of the alkaline earths, in which case an acid-resisting lining in the evaporating vessel is unnecessary. To the concentrated liquor sulphuric, hydrochloric or oxalic acid or an acid salt is added to improve the colour of the product formed, which product is somewhat hygroscopic and contains a compound resembling dextrin and which the author has called "dextrone". To obtain this product soluble salts, as the sulphate or chloride of sodium, etc., are added to the boiling liquor as long as the dextrone separates out, which, rising to the surface, may be easily removed. When cold this substance is a semi-solid and may be either dissolved in water or dried and reduced to a powder. Mixed with gelatin or glue it forms a substance similar to the gela-lignosin described by Messrs. Cross and Bevan, and, like that compound when dissolved in a suitable solvent, as sulphite of soda, can be employed as a mordant or size for textile fabrics, paper, etc. The liquor remaining after removing the dextrone may be further employed for the production of the gela-lignosin-like substance by adding a concentrated solution of glue or gelatin as long as the compound separates out.

English Patent 20036 (1893).
Austrian Privilegium 569 (1894).
J. Soc. Chem. Ind. vol. 3 (1894) p. 1085.

Ekman, C. D.—PROCESS FOR PRODUCING DEXTRONE FROM THE WASTE SULPHITE LIQUOR.

When the liquor is made alkaline and evaporated to a specific gravity of 1·315 at 85° C. a substitute for dextrine (dextrone) is obtained. This consists, when magnesium salts are used, of a mixture of magnesium sulphate and lignosulphonic magnesium (used as a mordant).

German Patent 81643 (1893).
See English Patent 20036 (1893).
Ber. vol. 28 (1896) p. 711.

Ekman, C. D.—WASTE SULPHITE LIQUOR.

Review of method for utilization. Process for manufacture of dextrone patented by the author. Liquor first evaporated to a very thick liquid. When a suitable salt is added the dextrone floats on the top as a paste. It is said that cloth treated with this dextrone will not be affected by damp or mildew, as is the case with ordinary dextrine.

Papier-Ztg. vol. 21 (1896) part I pp. 2218, 2609, 3247.
J. Soc. Chem. Ind. vol. 15 (1896) p. 735.

Mitscherlich, A.—REPLY TO EKMAN'S STATEMENTS.

Papier-Ztg. vol. 21 (1896) pp. 2349, 2850.

Seidel, H.—MORDANTING OF FIBROUS MATERIALS.

" The improvement consists in the use, as an assistant to metallic mordants, of the substance salted out from the lyes of sulphite-cellulose stuff by salts of the alkalies or alkaline earth metals; or the lye itself may be used for this purpose in more or less concentrated or purified condition. This substance is claimed to be a useful substitute for tartaric or lactic acid in the mordanting of wool with potassium bichromate."

English Patent 19005 (1897).
German Patent 9982 (1897).
J. Soc. Chem. Ind. vol. 17 (1898) p. 45.

Raaz, A.—LIGNOROSIN (CALCIUM LIGNOSULPHONATE). NEW REDUCING AGENT FOR CHROMIC ACID IN WOOL MORDANTING.

This compound, stated to be calcium lignosulphonite is a by-product of one of the processes of manufacturing paper pulp. It appears in commerce in the form of a dark brown syrup and is found to serve in many cases as an efficient substitute for lactic acid in mordanting wool with chrome. Dye trials were made with wool mordanted with 2·7 per cent of lignorosin, 1·26 per cent of potassium bichromate and 0·66 per cent of sulphuric acid. Mordanting is complete after an hour's boiling, the whole of the chromium being absorbed and the fibres affected no more than they are with a mixture of potassium, lactic acid, and sulphuric acid.

The wool mordanted as described has a pale brown colour, which renders it unsuitable for dyeing colours such as pale blues, greens, and pinks. The author is indebted to a paper by H. Seidel for the information that colours dyed on wool mordanted by the aid of lignorosin are as fast as usual to water, soap, alkalies, and acids. Their fastness to light has not yet been determined but no doubt is entertained that this will be found satisfactory too.

Farber-Ztg. vol. 9 (1898) p. 245.
J. Soc. Chem. Ind. vol. 17 (1898) p. 923.

Seidel, H.—WASTE LIQUOR FROM SULPHITE WOOD-PULP. (MORDANTING WOOL).

The author's invention for using these liquors, under the name of lignorosin, as an assistant to take the place of tartaric or lactic acid in mordanting wool, with bichromate, has already been noticed and has been patented. Some details of laboratory experiments are given in the paper. In comparison with lactic acid which utilizes the bichromate quite as well as lignorosin, the latter has the advantage of reducing it more slowly and is besides hardly one-third the price. Some loose wool dyed with alizarin on lignorosin and bichromate mordant and then milled three hours in acid of 4° Bé, with white wool did not bleed in the least on to the white. Formulae are given for dyeing wool.

Rev. gen. mat. color vol. 2 (1898) p. 370.
J. Soc. Chem. Ind. vol. 17 (1898) p. 1048.
Papier-Ztg. vol. 23 (1898) part II p. 2812.
Chem.-Ztg. vol. 22 (1898) p. 665.

Seidel, H. and Hanak, L.—WASTE LIQUOR FROM SULPHITE WOOD-PULP.

According to the Badische Anilin and Soda Fabrik, violet-black to black shades are produced on vegetable fibres by the products obtained by reducing 1·1 dinitronaphthalene with glucose in an alkaline solution (English Patent 20,250 of 1896; J. Soc. Chem. Ind. vol. 16 (1897), p. 582). By carrying out the reduction in presence of alkaline sulphites or bisulphites a water-soluble dyestuff is obtained, which dyes from an acid bath. By substituting sulphite liquor for the glucose, the authors have obtained lilac shades on cotton and dark violet on wool. For example, 10 grammes of 1·1 dinitronaphthalene, 900 c.c. of water, 200 c.c. of sulphite lye, 20 grammes of sodium bisulphite (38° Bé) and 20 grammes of soda lye (30° Bé) are heated on the water-bath until completely dissolved. The greenish-blue solution is made acid with hydrochloric acid and boiled until free from sulphurous acid. The dyestuff can be precipitated with alcohol. It dissolves in ammonia with a bluish-velvet colour, and dyes wool dark violet from an acid bath. In a like manner, 1·4 dinitronaphthalene gives a brown dye-stuff. With regard to the employment of waste sulphite liquor in the indigo vat, experiments have been carried out on a manufacturing scale, employing the following quantities: 2·283 kilogrammes (5·03 pounds) of indigo (java, 80 per cent) (ground with soda-lye, 1 part indigo, 3 parts water), 3·75 kilogrammes (8·25 pounds) of lime (slacked), 2·5 kilogrammes (5·5 pounds) of calcined soda, and 10 kilogrammes (22 pounds) of sulphite liquor (28° Bé) are brought up to 62·5 litres (13·8 gallons) and heated with direct steam until a reaction suddenly commences at 75°C. The vat is then made up to 500 litres (110 gallons), the diluting water being treated with 10 kilogrammes (22 pounds) of sulphite liquor, 3·75 kilogrammes (8.·25 pounds) of lime, and 2·5 kilogrammes (5·5 pounds) of calcined soda. Samples of the shades obtained are given in the paper.

UTILIZATION OF SULPHITE LIQUOR AS A WOOL MORDANT.

The most important wool mordant is, without a doubt, potassium bichromate. which requires a second mordant, tartaric acid. The employment of this latter has certain drawbacks, viz. its cost, and the fact that the whole of the bichromate is not utilized but partly runs to waste. The latter is remedied by using a mixture of lactic acid and sulphuric acid in place of the tartaric acid. Bearing in mind that lactic acid and tartaric acid act as reducing agents on potassium bichromate the authors have employed sulphite liquor with complete success as a mordant, together with potassium bichromate. The liquor is exactly neutralized and evaporated in a vacuum to 30° Bé. It is brought on to the market under the name of "lignorosin" and forms a dark brown syrup of 30° Bé., miscible with water and containing 50 per cent of solid matter, principally calcium lignin sulphonate; 6·2 per cent of ash, 4 per cent of organic sulphur, and only traces of sulphurous acid. When used as a mordant it is necessary to add sulphuric acid in such quantity as is equivalent to the potassium of the bichromate and the calcium of the lignorosin. On the large scale it has been found that in presence of sulphuric acid 1 kilogramme (2.2 lb.) of lignorosin will replace the same weight of lactic acid. Tables are given showing comparative tests with lignorosin and dyed patterns of some of the shades produced, compared with those obtained with tartaric acid and lactic acid.

Mitt. Techn. Gew. Mus. vol. 8 (1898) p. 348.
J. Soc. Chem. Ind. vol. 17 (1898) p. 844.

2nd International Congress Appl. Chem. Vienna 1898.—

From dinitronaphthalene a brown dyestuff may be obtained with the dry residue of sulphite liquor as also with dextrose.

Oesterreichischer Verein fur Cellulosefabrikation.—PROCESS FOR DYEING AND PRINTING WITH INDIGO, USING SULPHITE LIQUOR.

Sulphite liquor is used as a reducing agent to change indigo into indigo white. One kilogramme (2·2 lb.) of indigo is heated with 10 kilogrammes (22 lb.) of sulphite liquor (20° Bé), 20-50 kilogrammes (44-110 lb.) of Ca $(OH)_2$, and the same quantity of soda in 100 litres (22 gallons) of water by indirect steam. For printing, the cloth is treated with sulphite liquor and printed with a mixture of indigo, caustic soda-solution, and a thickening agent. The reduction is carried out by steam heating.

German Patent 104359 (1898).
Chem. Zentr. (1899) part II p. 1077.

Erste Oesterreichische Sodafabrik.—PROCESS FOR PREPARATION OF DYESTUFF FROM WASTE SULPHITE LIQUOR WHICH COLOURS COTTON DARK BROWN.

The liquor is heated with alkalies and sulphur and thereby made into an amorphous water-soluble mass.

Austrian Patent 2336 (1889).

Phelps, E. B.—THE POLLUTION OF STREAMS BY SULPHITE PULP WASTE.
(See " General " p. 185.)

Alt, H.—LIGNOROSIN MORDANT FOR WOOL.

Lignorosin does not reduce as quickly as lactic acid but faster than argol. The fastness to light changes with the nature of the dye.

Farber-Ztg. vol. 10 (1899) p. 303.
Jahrb. Chem. Techn. (1899) p. 972.

Kielmeyer, A.—LIGNOROSIN.

Lignorosin has the fault that it does not reduce chromic acid and the fabrics produced are not fast to light.

Farber-Ztg. (1899) p. 34.
Jahrb. Chem. Techn. (1899) p. 972.

Seidel, H.—LIGNOROSIN.

Seidel finds that lignorosin is almost completely used up by the potassium bichromate and sulphuric acid. The shades are as fast and intense as those from tartar or lactic acid. Kielmeyer (Farb. Zeit. page 103) does not agree with this.

Farber-Ztg. vol. 10 (1899) p. 68.

Seidel, H. and Pollak, J.—LIGNOROSIN.

Without a doubt lignorosin reduces chromium trioxide. The reduction is gradual and increases with the length of the mordanting process. They consider it a better reducing agent than tartar and fully equal to lactic acid.

Farber.-Ztg. vol. 10 (1899) p. 321.
Jahrb. Chem. Techn. (1899) p. 972.

Seidel, H.—LIGNOROSIN FREE FROM LIME.

Kielmeyer attributes to the presence of calcium in lignorosin (J. Soc. Chem. Ind. vol. 17 (1898) p. 923) a deleterious influence upon the mordanting of wool with the aid of this product. In regard to this it is asserted that the product as it is now manufactured contains on the average only 0·245 per cent of lime (CaO), which is insufficient to have any appreciable effect upon the mordanting in view of the fact that the product for use is diluted with 750 parts of water. The amount of lime present in the diluted solution corresponds with a hardness of 0·33° (German scale).

Mitt. Techn. Gew. Mus. (1900) vol. 10 p. 158.
J. Soc. Chem. Ind. vol. 19 (1900) p. 896.

Schwalbe, C. G.—LIGNOROSIN HAS PROVED A FAILURE.
Kolloid Z. vol. 5 (1909) p. 129.

Stutzer, A.—WASTE SULPHITE LIQUOR AS A MORDANT.

The author has succeeded in weakening the colouring matter in the waste liquor so that it may be used as a mordant for certain purposes.

Report on Annual Meeting of German Pulp and Paper Chemists (1910) pp. 50, 73, 75.

Badische Anilin und Soda Fabrik.—PROCESS FOR OBTAINING A FINE SUSPENSION OF DYESTUFFS WHICH ARE INSOLUBLE IN WATER.

Waste sulphite liquor is used. Press-cakes of dyestuffs (like indanthrene, etc.) can easily be obtained in a fine suspension by use of waste sulphite liquor. Only part of 1 per cent is required.

German Patent 222191 (1909).
Chem.-Ztg. vol. 34 (1910) Rep. p. 271.
Wochbl. Papierfabr. vol. 41 (1910) p. 2612.

Badische Anilin und Soda Fabrik.—PROCESS FOR OBTAINING FINE SUSPENSION OF DYESTUFFS INSOLUBLE IN WATER.

In the case of leuco compounds of the indigo and thio-indigo series the leuco solutions of the dyestuff are blown out slowly in the cold so that an oxidation only and no precipitation of dyestuff takes place.

German Patent 265536 (1912).
Addition to German Patent 222191 (1900).

Stutzer, A.—REMOVAL OF COLOURING MATTER FROM SULPHITE LYE.

A sufficient quantity of an alkaline-earth carbonate is added to the waste liquors to neutralize the stronger acids, the mixture is filtered, and a small quantity of phosphoric acid (e.g. 0.01 per cent) is added to the filtrate, which is then evaporated and filtered from the separated colouring matters, again evaporated, and mixed with sufficient calcium carbonate to remove the free phosphoric acid. It is stated that the greater part of the colouring matter is in this way removed from the liquors, rendering them suitable for use in dressing textiles or for sizing with tanning extracts.

German Patent 246658 (1911).
Z. angew. Chem. vol. 25 (1912) p. 1752.
J. Soc. Chem. Ind. vol. 31 (1912) p. 871.

Stutzer, A.—EXPERIMENTS ON REMOVAL OF COLOURING SUBSTANCES FROM WASTE SULPHITE LIQUOR.

Humus substances, chlorophyll decomposition products, tannic decomposition products, act as colouring matters. The colour is made lighter by addition of phosphoric acid 1 kilogramme (2.2 lb.) to 1 cub. m. (220 gallons) of liquor. By concentration a red dyestuff is precipitated. The phosphoric acid is also rendered insoluble and can be precipitated with chalk.

Papier-Ztg. vol. 36 (1911) p. 3450.

Lichtenstein, L.—PRINTING WITH HYDRONE AND SULPHUR DYESTUFFS.

In order to fix these dyestuffs waste sulphite liquor is added to the required solution salt.

Chem.-Ztg. vol. 36 (1912) Rep. p. 658.

Lichtenstein, L.—THE EFFECT OF WASTE SULPHITE LIQUOR UPON VAT DYESTUFF.

Hydron white was kept in fine suspension by the sulphite liquor. The liquor increases the capillary ascent of the dyestuff and reduces the absorption. By pressing tests with hydron dyes with addition of waste liquor and starch the waste liquor prevented the absorption of hydron white. The waste liquor acts as a protective colloid.

Farber-Ztg. vol. 24 (1913) p. 442.
Chem. Zentr. vol. 8 (1913) part II p. 2181.
Chem. Abs. vol. 8 (1914) p. 2064.

Walker, W. O.—THE PROBLEM OF THE WASTE LIQUOR FROM SULPHITE-PULP MILLS.

Phelps, of the United States Geological Survey, carried on a series of experiments to determine if condensation products could be obtained by treating the liquor with aromatic amines. These experiments were based on the assumption that aldehyde groups are present in the organic part of the liquor. He found that, of the amines tried, those retaining the NH_2 group gave bright red products, and those in which substitution had taken place in the NH_2 group gave brown or black compounds. Attempts to diazotise these products failed. When nitrated they gave different coloured products depending upon the amine used. Some of these substances were brilliant dyes. These reactions were carried out without purifying the original amine condensation products. Phelps failed to purify these as he was unable to prevent their decomposition.

McRae, of Queen's University, Kingston, Ontario, succeeded in preventing this decomposition in the case of aniline by treatment with bromine. He also showed that substitution had taken place in the amino group of the amine molecule, thus indicating the presence of a free carbonyl group in the original molecule. Phelps obtained a yellow dyestuff by treating the liquor with nitric acid. He failed to learn the structure of this body. It was found that the dyestuff could not be manufactured economically.

J. Soc. Chem. Ind. vol. 32 (1913) p. 389.
(See " General " p. 185.)
Paper vol. 11 (1913) No. 9 p. 21.

Phelps and McRae.—INVESTIGATION ON PREPARATION OF DYESTUFFS FROM WASTE SULPHITE LIQUOR.

Report on investigations on preparation of condensation products from waste liquors with aromatic amines. With amines containing the group NH_2 clear, red products were obtained. Amines in which substitution had taken place in the NH_2 group gave brown or black compounds. Azo products could not be obtained. By nitration various compounds are formed, depending on the amino compound used. Also, a yellow dyestuff was obtained with nitric acid, the production cost of which, however, was too high.

J. Soc. Chem. Ind. vol. 32 (1913) p. 389.

Oman, E.—LIGNIN AND LIGNONE DERIVATIVES.

(See " Miscellaneous " p. 168.)

DYESTUFFS FROM WASTE SULPHITE LIQUOR.

Two methods of research open to the chemist, viz:—

(1) Fusion with sulphur and sodium sulphide to form a sulphur dye.

(2) Coupling up with an amine and nitrating the mixture. General discussion of dyestuffs from Waste Sulphite Liquor.

Paper-Making vol. 36 (1917) p. 351.

SULPHUR

Pictet, R. P.—PROCESS FOR THE PREPARATION OF WOOD CELLULOSE BY THE USE OF SULPHUROUS ACID.

The patent claim protects a special apparatus. The further recovery of sulphurous acid and evaporation of the liquid are mentioned.

German Patent 26331 (1883).

Frank, A.—PROCESS FOR PURIFICATION OF CALCIUM SULPHITE OBTAINED THROUGH TREATING WASTE LIQUOR WITH LIME.

Purified by washing the precipitated $CaSO_3$, which is contaminated by organic substances, with dilute sulphurous acid or a calcium bisulphite solution. The purified $CaSO_3$ can be used afresh.

German Patent 40308 (1886).
Ber. vol. 20 (1887) p. 667.
Papier-Ztg. vol. 12 (1887) p. 1170.

Frank, A.—IMPROVEMENTS RELATING TO THE SPENT LYES OF SULPHITE PROCESS.

The lyes resulting from the manufacture of cellulose, paper pulp, textile fibres, etc., by the sulphite process contain sulphurous acid, some of which is free while some is in the form of sulphites and bisulphites. The present invention relates to the removal and recovery of the sulphites from the lyes, so that the remaining solution can be utilized for forage and manuring purposes. When the lyes contain lime or magnesia as a base, a quantity of caustic lime is added, equivalent to the proportion of sulphurous acid present. When the lyes contain the sulphite or bisulphite of soda or potash, a mixture of calcium chloride and lime is added, so that the amount of calcium chloride is equivalent to the alkali while the lime is in proportion to the sulphurous acid present. In every case the sulphurous acid is precipitated as calcium monosulphite, which is separated from the lyes by filter presses. The organic matter still adhering to this precipitate is removed by elutriation with water, to which neutral salts (sodium or calcium chloride) can be added to increase the specific gravity. The calcium monosulphite owing to its greater specific weight thereby separates from the lighter organic substances; or the purification may be effected by washing the precipitate with a highly diluted solution of sulphurous acid or with a solution of calcium bisulphite, in either of which solutions the organic substances are soluble. The purified calcium monosulphite is worked up for producing fresh solutions of bisulphites by either of the following processes:—

1. It is stirred up in an aqueous solution of sulphurous acid;

2. The monosulphite is treated with sufficient dilute sulphuric acid to combine with a part of the lime, the lime forming calcium sulphate (annalin, pearl hardening) whilst the sulphurous acid, which has thus become free, changes the undecomposed monosulphite into a solution of bisulphite of the desired composition; or

3. The monosulphite is introduced into a solution of sodium bisulphate, whereby a precipitate of calcium sulphate and a solution of sodium bisulphite is obtained. Owing to the use of caustic lime for the precipitation of the monosulphites from the lyes, these solutions will have an alkaline reaction which makes them unfit for use as forage and manure. It is, therefore, of advantage to pass carbonic acid and air through the solution to precipitate the caustic lime and oxidize the last traces of the sulphite still dissolved. If the use as manure be intended a quantity of acid phosphate of lime is added sufficient for forming a basic phosphate with the caustic lime present.

English Patent 13286 (1886).
Austrian Patent 646 (1887).
J. Soc. Chem. Ind. vol. 6 (1887) p. 735.

Frank, A.—PREPARATION AND RECOVERY OF SULPHUROUS ACID IN THE SULPHITE PROCESS.

Precipitation of monosulphite with milk of lime. Irrigation of meadows with the purified liquor.

Papier-Ztg. vol. 12 (1887) pp. 1765, 1782, 1832, vol. 13 (1888) p. 531.
Polytechn, J. vol. 268 p. 485, vol. 276 p. 58.
Hofmann, C., Handbuch der Papierfabrikation 2nd edition (1897) p. 1597.

Frank, A.—PREPARATION OF SULPHITE LIQUOR ACCORDING TO THE CONSUMPTION AND RECOVERY OF SULPHUR.

Papier-Ztg. vol. 14 (1889) p. 1488.

Chemische Fabrik Grünan, Landshoff and Meyer.—PROCESS FOR PRODUCTION OF ALKALI SULPHATES AND CALCIUM SULPHITE FROM LIQUORS CONTAINING ALKALI SULPHITE, BY MEANS OF CALCIUM SULPHATE.

The sulphurous acid from waste sulphite liquors can be recovered in the calcium sulphate after neutralization with lime according to the description of the patent.

German Patent 48269 (1888).
Papier-Ztg. vol. 14 (1889) p. 2310.

Maschinenbauanstalt Golzern.—APPARATUS FOR UTILIZATION OF THE SULPHUROUS ACID FROM WASTE SULPHITE LIQUORS IN PREPARING CALCIUM BISULPHITE SOLUTION.

The waste liquor is neutralized with milk of lime; the precipitate of calcium sulphite is transformed into bisulphite liquor by use of sulphurous acid coming from the digester.

German Patent 69892 (1893).
Ber. vol. 26 (1893) p. 973.
Papier-Ztg. vol. 48 (1893) pp. 1736, 2662.

Drewsen, V.—PROCESS FOR PURIFICATION AND UTILIZATION OF WASTE SULPHITE LIQUOR.

The liquor is treated with caustic lime at a temperature above 100°C. preferably at 90 pounds steam pressure. The precipitate is dissolved with sulphurous acid and the remaining organic substance is separated off.

German Patent 67889 (1891).
English Patent 2629 (1892).
Ber. vol. 26 (1893) p. 538.
J. Soc. Chem. Ind. vol. 12 (1893) p. 461.
Papier-Ztg. vol. 18 (1893) p. 1289.

Kumpfmiller, A., and Schultgen, E.—PROCESS FOR CONCENTRATING WASTE SULPHITE LIQUOR AND RECLAIMING THE FREE AND COMBINED SULPHUROUS ACID.

German Patent 81338.
(See " Evaporation " p. 162.)

umpfmiller, A., and Schultgen, E.—PROCESS AND APPARATUS FOR CONCENTRATING WASTE SULPHITE LIQUOR.

German Patent 83438 (1894).
Austrian Privilegium 5849 (1894).
(See " Evaporation " p. 162.)

Wichelhaus, H.—EXAMINATION OF WASTE SULPHITE LIQUORS AND WASTE WATERS FROM SULPHITE MILLS.

Recovery of SO_2 by neutralizing with lime. Oxidation of organic substances by air.

(See " Effluents " p. 35.)

Blackman, B.—UTILIZATION OF LIQUOR.
United States Patents 369836, 530634, 530635 (1895).
(See Tanning Materials" p. 78.)

Hofmann, C.—HANDBUCH DER PAPIERFABRIKATION.
2nd Edition (1897) pp. 1575, 1597.

Dorenfeldt, L. J.—FURNACE FOR BURNING WASTE SULPHITE LIQUOR AND RECLAIMING THE SULPHUR.

Liquor neutralized with soda evaporated to dryness, calcium carbonate added and ignited, and the soda recovered by leaching. From the remaining calcium sulphite the sulphur and calcium are reclaimed by treatment with CO_2 in the presence of water.
German Patent 113435 (1898).
Austrian Privilegium 3807 (1898).
Papier-Ztg. vol. 25 (1900) part II p. 2916.
Chem. Zentr. (1900) part II p. 702.

Turk, G.—APPARATUS FOR CONDENSATION OF RELIEF GASES FROM THE SULPHITE DIGESTERS.

Use of a gas compressor.
German Patent 115607 (1899).
Jahrb. Chem. Techn. (1900) part II p. 530.

Dorenfeldt, L. J.—PROCESS FOR UTILIZATION OF SULPHITE LIQUOR.

The residue from the burning of liquor from the sodium bisulphite process is extracted. The filtrate is treated with CO_2 and S is removed from H_2S which is driven off. The sodium bicarbonate solution is treated with an equivalent quantity of $NaHSO_3$, the CO_2 is recovered, and the sodium sulphite liquor thus formed is treated with fresh SO_2 to form $NaHSO_3$.
German Patent 129227.
Chem. Zentr. (1902) part I p. 686.

Trippe, W.—UTILIZATION OF SULPHITE LIQUOR, RECOVERY OF SULPHUR.

Various organic substances e.g. albuminoid, terpenes, resins, and tar products are added to the liquor, which on evaporation cause the sulphur compounds to decompose at a lower temperature, so that carbonisation is avoided.
German Patent 133312 (1901).
Chem. Zentr. (1902) part II p. 410.

Brookes, A. G.—TREATMENT AND UTILIZATION OF SULPHITE WASTE LIQUOR.
English Patent 8088 (1901).

Bucherer, H.—WASTE SULPHITE LIQUOR.

Discussion of Frank's process of treating the waste liquor with milk of lime.
Papier-Ztg. vol. 30 (1905) part I p. 1350.
Z. angew Chem. vol. 17 (1904) p. 31.

Morterud, E.—PROCESS FOR OBTAINING GAS AND HEAT IN THE MANUFACTURE OF SULPHITE PULP.
German Patent 180168 (1905).
Austrian Patent 638 (1905).
United States Patent 833936 (1906).
(See "Miscellaneous" p. 168.)

Simonson.—UTILIZATION OF LIME SLUDGE FROM SULPHITE MILLS.
Swedish Patent 28551 (1907).

Sollbrig.—NEW PROCESSES IN THE MANUFACTURE OF SULPHITE PULP RECLAIMING OF SULPHUROUS ACID.

Papier-Fabr. vol. 5 (1907) p. 5.

Kumpfmiller, A.—RECOVERING SULPHUROUS ACID AND CALCIUM SULPHITE FROM WASTE SULPHITE LIQUOR.

German Patent 203648 (1906).
Chem. Abs. vol. 3 (1909) p. 714.
J. Soc. Chem. Ind. vol. 27 (1908) p. 1174.

Shelvin and Small.—CONDENSER FOR WASTE LIQUOR AND GAS FROM CELLULOSE DIGESTERS.

United States Patent 880247 (1908).
Chem.-Ztg. vol. 32 (1908) Rep. p. 347.

Brunet, L.—PURIFYING AND CONCENTRATING SULPHITE LYES.

French Patent 459069 (1912).
(See "Evaporation" p. 162.)

Dickerson, W. H.—TREATMENT OF SULPHITE LIQUORS.

In order to prevent the decomposition of waste sulphite liquors during evaporation, a part of the basic constituents is precipitated with sulphuric acid and the solution kept acid. Another method is to concentrate in an acid state in the presence of soluble barium salts.

United States Patent 1059716 (1913).
J. Soc. Chem. Ind. vol. 32 (1913) p. 531.

Griffin, M. L.—RECOVERY OF WASTE PRODUCTS.

Evaporation and ignition of the waste liquor, whereby sulphides are formed. Alkali sulphide is washed out. Decomposition of the sulphite of alkali earth with CO_2. Transformation of hydrogen sulphide to sulphur dioxide which is used for preparing sulphite liquor.

Paper Trade J. Conv. Number (1911).
Paper-Maker Brit. Trade J. vol. 17 (1911) No. 1 p. 55.

Schneider, F. and Graf, G.—PROCESS AND ARRANGEMENT FOR PURIFICATION OF WASTE SULPHITE LIQUOR BY TREATMENT WITH LIME, AIR, AND CARBON DIOXIDE.

The liquor is treated continuously in the order mentioned and the precipitated matters recovered. Special apparatus described.

German Patent Appl. Sch. 36744 (1910).
Papier-Fabr. vol. 9 (1911) p. 827.

Stutzer, A.—PROCESS FOR ELIMINATING THE SULPHUROUS ACID IN WASTE SULPHITE LIQUORS.

Treatment of the hot liquor with hydroxide or carbonate of ammonia. A previous treatment with calcium carbonate neutralizes stronger acids (sulphuric). With this previous treatment 10 c.c. of a 10 per cent ammonia solution are required per litre of waste liquor. Without previous treatment 30 c.c. are required.

German Patent 236035 (1909).
Papier-Fabr. vol. 9 (1911) p. 858.
Chem. Abs. vol. 5 (1911) p. 3622.

Farbenfabriken vorm. Friedr. Bayer.—PROCESS FOR MANUFACTURE OF SULPHUR AND SULPHATES FROM OXYGEN COMPOUNDS.

Liquors containing sulphites and bisulphites, alone or in mixture with thiosulphates, are heated with polythionates.

German Patent 264920 (1912).

Farbenfabriken vorm. Friedr. Bayer.—PROCESS FOR MANUFACTURE OF SULPHUR AND SULPHATES BY HEATING SULPHITES UNDER PRESSURE.

Mixture of acid and neutral sulphites are used.

German Patent 265167 (1912).

Thorne, C. B.—PROCESS FOR PREPARING COOKING LIQUOR FROM THE RELIEF GASES BY RECLAIMING THE SO_2 GASES AND CONDENSED SO_2 SOLUTIONS.

United States Patent 1076078 (1912).
German Patent 291854 (1913).
Norwegian Patent 26445 (1915).
Chem. Abs. vol. 11 (1917) p. 1546.
Papir. J. vol. 4 (1916) p. 22.
Pulp Paper Mag. Can. vol. 15 (1917) p. 677.

Lehmann, E.—PROCESS AND APPARATUS FOR CONCENTRATING LIQUORS, ESPECIALLY WASTE SULPHITE LIQUORS, WHICH LEAVE THE DIGESTER IN A BOILING STATE UNDER PRESSURE.

German Patent Application L. 35694 (1912).
German Patent 282951 (1912).
Norwegian Patent 24561 (1913).
(See "Evaporation" p. 162.)

Schutz, G. A.—PROCESS FOR REMOVAL OF GASES FROM SOLUTIONS BY HEATING.

During the heating the solutions are brought in contact with substances which are porous or have rough surfaces.

German Patent Application Sch. 39465 (1911).

Strehlenert, R. W.—SULPHUR FROM WASTE SULPHITE LIQUOR.

In the Strehlenert fuel process 5-6 grammes of SO_2 are recovered per litre of waste liquor (0.05-0.06 lb. per gallon).

Svensk. Kem. Tid. (1913) p. 78.
Chem.-Ztg. vol. 37 (1913) p. 605.
Wochbl. Papierfabr. vol. 44 (1913) p. 4142.
(See "Fuel" p. 126.)

Ellis, C.—PROCESS FOR CONCENTRATING WASTE SULPHITE LIQUOR.

Part of the free SO_2 is removed by aeration and the rest neutralized with lime. In order to obtain hydrolysis hot air is blown through at 60°. Liquor filtered, evaporated in vacuo and again filtered.

United States Patent 1057416 (1913).
J. Soc. Chem. Ind. vol. 31 (1912) p. 1120; vol. 32 (1913) p. 482.

Muller, M.—RECOVERY OF SULPHUROUS ACID BY EVAPORATION OF WASTE SULPHITE LIQUOR.

The removal of SO_2 takes place simultaneously with the evaporation below 70° in order to facilitate the absorption of the gas.

German Patent 241282 (1911).
(See "Evaporation" p. 162.)

Stutzer, A.—PROCESS FOR RECOVERY OF SO_2 FROM SULPHITE LIQUOR.

The hot liquor is treated with NH_4OH or $(NH_4)_2CO_3$, until the reaction is alkaline. The liquor is filtered and concentrated. The sulphurous acid is in three forms, viz. as calcium bisulphite, as derivative of carbohydrate aldehydes and ketones, and as lignosulphonic acid. To use the organic material it is necessary to get rid of the bisulphite and to drive off the SO_2 loosely combined. While this can be done with strong acids or alkalies, yet the lignosulphonic acid is partially attacked. The use of ammonia avoids this.

German Patent Application St. 14656 (1909). See German Patent 236035 (1909).
Z. angew. Chem. vol. 23 (1910) p. 2357.
Chem. Zentr. (1911) part II p. 246.

Achenbach, H.—PROCESS FOR RECOVERY OF SO_2 FROM SULPHITE LYES.

The pipe through which the liquor passes after leaving the digester is provided with an atomizing device enclosed in a closed chamber, and the liquor is atomized by means of its own pressure. The sulphurous acid thereby evolved and the residual liquor are led off from the closed chamber through separate outlets.

German Patent 252412 (1911).
J. Soc. Chem. Ind. vol. 31 (1912) p. 1120.
Chem. Abs. vol. 7 (1913) p. 416.

Necas.—THE RECOVERY OF SULPHUR DIOXIDE FROM WASTE SULPHITE LYES.

A cylindrical vessel with its axis horizontal holding about 3 cubic metres (600 gallons) and divided into two compartments by a vertical partition. The fresh lime from the towers or vats, that has to be enriched by the waste gas from the pulp boilers, enters the first compartment of the apparatus from a vertical pipe, and at the same time the waste gases enter the compartment through a horizontal injector-like nozzle which sprays the lye through the gases against the vertical partition. The coal lye at once cools and absorbs the gases. The solution passes into perforated copper tubes in the second compartment and from there into the outlet pipe communicating with the reservoirs for the enriched lye. Increases in free acid from 3·16 to 5·12 per cent are obtained, and 75 per cent sulphur dioxide recovered.

Patent applied for.
Pulp Paper Mag. Can. vol. 11 (1913) p. 599.
Paper vol. 12 (1913) No. 10 p. 20.

Walther, R. von.—SULPHUR FROM SULPHITE LIQUOR.

The lye is treated with a quantity of hydrogen sulphite sufficient to decompose the sulphurous acid, and its compounds, present therein.

German Patent 262468 (1912).
J. Soc. Chem. Ind. vol. 32 (1913) p. 827.

Blockmann, R.—RENDERING SULPHITE-CELLULOSE LYES INNOCUOUS.

The hot waste lyes containing sulphurous acid are treated with a metal such as iron or zinc and a sufficient quantity of calcium carbonate or lime, or other base, to combine with the free acid. This treatment results in the reduction of the sulphur dioxide to hydrogen sulphide, which combines with iron, forming sulphide; the sulphurous acid is recovered from this by roasting.

German Patent 266122 (1912).
J. Soc. Chem. Ind. vol. 32 (1913) p. 1104.
Chem. Abs. vol. 8 (1914) p. 822.

Brunet, L.—CONCENTRATING WASTE SULPHITE LIQUOR.

The preheated liquor is sprayed in a tower and a current of hot air is passed through it, whereby the SO_2 undesirable for briquetting is converted into SO_3 which combines with the lime of the lye, whereupon the $CaSO_4$ is precipitated.

French Patent 459069 (1912).
Chem. Abs. vol. 8 (1914) p. 2805.

Achenbach, H.—PROCESS AND APPARATUS FOR RECOVERY OF THE SULPHUROUS ACID PRESENT IN THE WASTE SULPHITE LIQUOR.

Atomizing by means of its own pressure in a closed container.

Norwegian Patent 23689 (1913).
Papir J. vol. 1 (1913) p. 30.

Moore, H. K. and Wolf, R. B.—RECLAIMING SULPHUR DIOXIDE FROM SULPHITE LIQUOR.

The contents of the digester are discharged into a blow-pit provided with a vent which maintains the pressure substantially at that of the atmosphere. A surface condenser communicates with the vent, so that the absorption of the sulphur dioxide is limited to that taken up by the liquid products of condensation. The condensed liquid is collected and the excess of sulphur dioxide in the gases passed on for recovery.

United States Patent 1103216 (1914).
J. Soc. Chem. Ind. vol. 33 (1914) p. 859.
Chem. Abs. vol. 8 (1914) p. 3119.
Pulp Paper Mag. Can. vol. 12 (1914) p. 470.

Moore, H. K. and Wolf, R. B.—RECLAIMING SULPHUR DIOXIDE FROM SULPHITE LIQUOR.

In connection with a sulphite pulp digester a blow-pit is provided having a vomit stack with a removable cap and connected with a surface condenser. The blow-pit is filled with steam to expel the air and then connected with an air-pump; the contents of the digester are discharged into the pit, the vapours rising from which are condensed and the sulphur dioxide separated and removed.

United States Patent 1110454 (1914).
J. Soc. Chem Ind. vol. 33 (1914) p. 1006.
Pulp Paper Mag. Can. vol. 12 (1914) p. 533.
Paper vol. 15 (1914) No. 4 p. 22.

ATOMIZING OF PULP LIQUORS.

By this process a certain amount of sulphurous acid can be recovered.

Papier-Fabr. vol. 12 (1914) p. 969.

RECOVERY OF SULPHUROUS ACID FROM WASTE LIQUORS.

The liquors are atomized at a pressure higher than that of the digester.

Z. angew. Chem. vol. 27 (1914) p. 504.

Achenbach, H.—RECOVERING SULPHUR DIOXIDE.

When the pressure of the discharged lye is too low to effect the required atomizing this is reinforced, and the resulting vapour mixture immediately after its formation is thrown down by cooling and at the same time drawn off, whereby the removal of gas is facilitated and other advantages are obtained.

German Patent 286601 (1914).
Addition to German Patent 252412 (1911).
Chem. Abs. vol. 10 (1916) p. 2148.

Thorne, C. B.—RECLAIMING SYSTEM.

Pulp Paper Mag. Can. vol. 13 (1915) p. 173.
Chem. Abs. vol. 9 (1915) p. 1390.

Fest, A. D.—PROCESS FOR THE UTILIZATION OF WASTE SULPHITE LIQUOR.

The liquor is concentrated and treated by fermentation for the recovery of alcohol, and solid substances are precipitated from the residual solution. The precipitate is calcined, and the gases produced in calcination are passed in contact with a medium capable of extracting sulphur dioxide for the production of calcium bisulphite, a suitable medium consisting of the ashes of calcination in the presence of water.

United States Patent 1218638 (1917).
J. Soc. Chem. Ind. vol. 36 (1917) p. 451.
Chem. Abs. vol. 11 (1917) p. 1545.
Pulp Paper Mag. Can. vol. 15 (1917) p. 677.
Paper vol. 20 (1917) No. 11 p. 22.

Bergstrom, H. O. V.—UTILIZING WASTE GASES OF SULPHITE CELLULOSE MANUFACTURE FOR THE PRODUCTION OF DIGESTER ACID.

A suitable apparatus is specified.

German Patent 290680 (1914).
Norwegian Patent 27849 (1914).
Chem. Abs. vol. 11 (1917) p. 705.
Pulp Paper Mag. Can. vol. 15 (1917) p. 809.

Richter, A. F. and Dunbar, L.—RECLAIMING SULPHUR DIOXIDE.

United States Patent 1213414 and 1213415 (1917).
Chem. Abs. vol. 11 (1917) p. 888.

Muller, M.—PROCESS FOR UTILIZING WASTE SULPHITE LIQUOR.

Sodium bisulphate is roasted in a furnace under reducing conditions with waste sulphite liquor. The free sulphuric acid of the bisulphate is reduced to sulphurous acid which may be employed for the preparation of fresh sulphite liquor.

German Patent 297374 (1916).
J. Soc. Chem. Ind. vol. 36 (1917) p. 870.
Paper Makers' Monthly J. vol. 55 (1917) p. 303.

Kuhn, A. D. J.—RECOVERY OF SO_2 IN SULPHITE COOKING.

Deals with three different types of recovery system in sulphite cooking.

Wochbl. Papierfabr. vol. 47 (1916) pp. 2139, 2179, 2233, 2270.
J. Soc. Chem. Ind. vol. 36 (1917) p. 639.
Chem.-Ztg. vol. 41 (1917) Rep. p. 148.
Paper vol. 20 (1917) No. 24 p. 13.
Pulp Paper Mag. Can. vol. 15 (1917) pp. 857, 1009.

Landmark, H. B.—METHOD AND APPARATUS FOR RECOVERY OF FREE SO_2 FROM WASTE SULPHITE LIQUOR WITH SIMULTANEOUS CONCENTRATION OF THIS BY MEANS OF ITS LATENT HEAT.

Norwegian Patent 28147 (1917).
(See " Evaporation " p. 162.)

EVAPORATION

Novak, J.—PROCESS FOR EVAPORATION OF SULPHITE LIQUOR IN VACUO.

Liquor evaporated in multiple effects. This has not as yet been possible on account of the great foaming. This is overcome by saturating with quicklime, then with CO_2, and filtering off the precipitate.

German Patent 74031 (1893).
Ber. vol. 27 (1898) p. 474.
Papier-Ztg. vol. 19 (1894) p. 1196.

Kumpfmiller, A. and Schultgen, E.—PROCESS FOR CONCENTRATING WASTE SULPHITE LIQUOR AND RECLAIMING FREE AND COMBINED SULPHUROUS ACID.

The roast gases from the pyrites furnaces are conducted into the waste liquors which have not previously been neutralized. In this way the sulphuric acid is also removed from the roast gases. The waste liquor may afterwards be evaporated.

German Patent 81338 (1894).
Ber. vol. 28 (1895) p. 685.

Kumpfmiller, A. and Schultgen, E.—PROCESS AND APPARATUS FOR CONCENTRATING WASTE SULPHITE LIQUORS.

Vacuum evaporator on the counter-current principle in connection with German Patent 81338.

German Patent 83438 (1894).
Austrian Privilegium 5849 (1894).
Ber. vol. 28 (1896) p. 1030.

Seidel, H. and Hanak, L.—WASTE SULPHITE LIQUOR.

Various schemes have been proposed to render the sulphite liquor harmless, either by rendering the lye innocuous by evaporation, by recovering the sulphur or by utilizing for other purposes the organic substances formed from the non-cellulose portions of the wood in the boiling process. According to the first method, patents have been taken out in Germany for treating the liquor with lime, saturating with carbonic acid, and evaporating the filtrate in a vacuum or multiple-effect apparatus or else by employing a particular form of evaporating plant. The liquor is evaporated to about 30° Bé., when it contains more than 50 per cent of dry substance, and is mixed with wood shavings and burned. In order to effect this evaporation about nine times the quantity of water has to be evaporated compared to the dry substance obtained, and the calorific value of the fuel produced is only about 60 per cent of that of medium coal.

Mitt. Techn. Gew. Mus. (Vienna) vol. 8 (1898) p. 337.
J. Soc. Chem. Ind. vol. 17 (1898) p. 863.

Hofmann, C.—HANDBUCH DER PAPIERFABRIKATION.

2nd Edition (1897) 1628 pages.

Szamek, J.—PROCESS FOR BURNING ORGANIC SUBSTANCES IN LIQUORS.

The partially evaporated liquor (30° Bé.) is mixed with combustible absorbent substances (as sawdust, peat, cork, etc.) and burnt in open furnaces.

German Patent 130665 (1901).
Biedermanns Chem. Techn. Jahrb. (1901) p. 590.
Chem. Zentr. (1902) part I p. 1082.

Schwager, J.—EVAPORATION OF WASTE SULPHITE LIQUOR.

Heat necessary for evaporation of water as compared with sulphite liquor. Use of waste steam for evaporation of the liquor.

Papier-Ztg. vol. 28 (1903) part II pp. 2075, 2183.

Wernecke, E.—APPARATUS FOR CONCENTRATING LIQUIDS.

Continuous evaporation apparatus with direct heating with cups placed on the inside of the walls. The steam space has the form of an inverted cone so that the level of the liquid in the different cups decreases from top to bottom. It is possible by means of this apparatus to evaporate to high consistency by separate removal of liquor and vapours of various specific gravity.

German Patent 201372 (1907).

Kayser, H.—EVAPORATION OF WASTE SULPHITE LIQUOR.

(See " Binding Material " p. 52.)

Opitz & Kayser.—CELL-PITCH FROM WASTE SULPHITE LIQUOR.

(See " Binding Material " p. 52.)

Muller, M.—EVAPORATION OF WASTE SULPHITE LIQUOR.

(See " Binding Material " p. 52.)

Sembritzki, W.—MANUFACTURE OF CELL-PITCH FROM SULPHITE LIQUORS.

The success of the Walsum experiments is attributed in large part to the sextuple-effect Kestner evaporator used. Each effect has a heating surface of 55 sq. m. (592 sq. ft.), the first vessel is heated with steam at 3-4 atmospheres (45-60 lb. per sq. in.), and the boiling point in the last effect is 50° C. The liquor requires about three hours for its concentration to 35° Bé. This syrup is converted into solid pitch by two steam-heated drums which dip below its surface. The first drum concentrates the syrup from 35° to 60° Bé., the second drum converts it into a solid film which is removed by a scraper. Ten kilogrammes (22 lb.) of waste lye yield 1 kilogramme (2.2 lb.) of dry substance. It is stated that a selling price of 40 marks ($9.52) per metric ton (2,204 lb.) would show a good profit. This is equivalent to $8.64 per short ton.

Papier-Ztg. vol. 33 (1908) part I p. 872.
Wochbl. Papierfabr. vol. 39 (1908) p. 2866.
J. Soc. Chem. Ind. vol. 27 (1908) p. 915.
Chem. Abs. vol. 2 (1908) p. 3403.

Kestner, P.—PROCESS AND APPARATUS FOR CONCENTRATION OF EXTRACTS OR LIQUORS.

The liquors are forced, by means of the steam produced by the evaporation, at high speed through one or several heated pipes which are joined together, and at last leave the end of the pipe at a high velocity. The pipes are arranged almost vertically and are connected in series. At the point where the liquor enters the system a pump is placed, and at the lower end of the last pipe a steam separator is placed.

German Patent Application 46236 (1910).

Kestner, P.—EVAPORATION APPARATUS WITH LONG VERTICAL PIPES AND A CONTAINER FOR SEPARATION OF THE STEAM.

The pipes reach into the separation container to a little beneath the cover.

German Patent 226106 (1910).
Z. angew. Chem. vol. 23 (1910) p. 2282.

Kumpfmiller, A.—REPORT ON EVAPORATION OF AND DETERMINATION OF THE COEFFICIENT OF HEAT TRANSMISSION, "K" OF WASTE SULPHITE LIQUORS, AND THE USE OF THE LIQUOR FOR TANNING PURPOSES.

Report on Annual Meeting of German Pulp anl Paper Chemists 1910 p. 51.

Muller, M.—PROCESS FOR PURIFICATION AND EVAPORATION OF WASTE SULPHITE LIQUOR FOR USE AS FORAGE OR MANURE.

Lime is removed from the liquor by the addition of sodium sulphate. The liquor is then evaporated in vacuo whereby the SO_2 is driven off with the steam. The vapours are conducted through lime in which the SO_2 is absorbed. The remaining liquor is treated in the multiple-effect counter-current evaporator without any mechanical conveyance. The removal of SO_2 and the evaporation to the desired concentration may be effected simultaneously.

German Patent 241282 (1911).
Wochbl. Papierfabr. vol. 42 (1911) p. 4864.

Sudenburger Maschinenfabrik u. Eisengisserei.—APPARATUS FOR AUTOMATIC REGULATIONS OF THE STEAM INLET IN APPARATUS FOR HEATING AND EVAPORATING SOLUTIONS.

German Patent 266909 (1912).
Addition to German Patent 219294.

Liese, H. M.—PROCESS AND APPARATUS FOR THE UTILIZATION OF HEAT OF WASTE INDUSTRIAL WATER AND OTHER LIQUIDS.

The process is adapted for recovering heat from waste liquids containing suspended or dissolved matter which would deposit on cooking, and consists in bringing heat-exchanging surfaces into contact with steam generated from the liquid by a reduction of pressure, so that no deposit or incrustation is formed upon them. The waste liquid is passed through the lower portion of a series of chambers, in the upper portion of which are situated vessels or coils containing the liquid to be heated. The chambers are arranged so that a large surface of the liquid is exposed to the influence of the reduced pressure. The suction pipes are connected with the top of the chamber.

English Patent 1832 (1911).
J. Soc. Chem. Ind. vol. 30 (1911) p. 1441.

Buisson, J.—APPARATUS FOR EVAPORATING LIQUIDS, MORE PARTICULARLY PULP-MILL LIQUORS.

The vapours primarily obtained by the evaporation are again heated in order to evaporate fresh amounts of liquor.

French Patent 442809 (1912).
Chem.-Ztg. vol. 36 (1912) Rep. p. 69.
J. Soc. Chem. Ind. vol. 31 (1912) p. 1069.

ELLIS, C.—CONCENTRATION OF WASTE SULPHITE LIQUOR.

Concentrated sulphite liquor suitable for use as a binding material for road-surface is prepared by approximately neutralizing the waste sulphite liquor containing the diffusible constituents, separating the solid matters, aerating the liquid, fermenting it with yeast to remove the saccharine matter, separating volatile substances from the product, and concentrating the residue to a density of about 30° Bé. (specific gravity 1·263).

United States Patent 1042538 (1912).
J. Soc. Chem. Ind. vol. 31 (1912) p. 1120.

Brunet, L.—PURIFYING AND CONCENTRATING SULPHITE LYES.

The lyes are sprayed into the top of a tower up which a current of heated air is passed. The sulphurous acid compounds are thus oxidized and the lye is concentrated by evaporation, issuing at the bottom of the tower as a thick liquid containing calcium sulphate in suspension.

French Patent 459069 (1912).
J. Soc. Chem. Ind. vol. 32 (1913) p. 1153.

Ellis, C.—PROCESS OF CONCENTRATING SULPHITE WASTE LIQUOR.

The waste liquors are freed from a portion of the free sulphur dioxide by air-blowing, the remainder being neutralized with alkali. The alkaline liquor is then heated to promote hydrolysis, concentrated under reduced pressure, and finally freed from insoluble products of hydrolysis. It is recommended to blow air heated to 60°C. through the liquor heated to 40°C., make alkaline with lime, continue the aeration at 60°C., filter, concentrate, and again filter.

United States Patent 1057416 (1912).
J. Soc. Chem. Ind. vol. 32 (1913) p. 482.
Chem. Abs. vol. 7 (1913) p. 1806.
Pulp Paper Mag. Can. vol. 10 (1912) p. 372.

Dickerson, W. H.—METHOD OF TREATING LIQUORS CONTAINING SULPHUROUS ACID OR SULPHITES.

In order to prevent the decomposition of waste sulphite liquors during evaporation, a part of the basic constituents is precipitated with sulphuric acid and the solution kept acid. Another method is to concentrate in an acid state in the presence of soluble barium compounds.

United States Patent 1059716 (1913).
J. Soc. Chem. Ind. vol. 32 (1913) p. 531.
Chem. Abs. vol. 7 (1913) p. 2115.

Wolesky, F.—CONTINUOUS APPARATUS FOR EVAPORATION AND CONCENTRATION OF WASTE LIQUORS.

Papier-Ztg. vol. 39 (1914) p. 1008.

Rosenthal.—CONCENTRATION OF LIQUORS IN THE "STEP" EVAPORATOR.

Papier-Ztg. vol. 39 (1914) p. 1007.
Wochbl. Papierfabr. vol. 45 (1914) p. 1847.
Chem.-Ztg. vol. 38 (1914) p. 126.

Muller, M.—NEW SUGGESTIONS IN THE EVAPORATION AND PREPARATION OF WASTE LIQUORS FROM THE INDUSTRY.

Wochbl. Papierfabr. vol. 45. Annual Number (1914) p. 2276.
Chem. Abs. vol. 8 (1914) p. 3119.

Kennard, F. H.—PROCESS OF REDUCING WASTE SULPHITE LIQUOR TO A POWDER.

The waste liquor is concentrated to a viscous state in vacuo and the product is applied in the form of a thin film to a heated surface also in vacuo, being retained thereon until it is dry.

United States Patent 1138118 (1915).
J. Soc. Chem. Ind. vol. 34 (1915) p. 656.
Chem. Abs. vol. 9 (1915) p. 1691.
J. Ind. Eng. Chem. vol. 7 (1915) p. 1008.

Lehmann, E.—CONCENTRATION OF LYES, ESPECIALLY SULPHITE CELLULOSE WASTE LYES.

The hot waste lye is discharged under pressure from the digester, through a pipe, into a vessel where a lower pressure prevails. The steam evolved escapes at the upper part of the vessel and the residual liquor is drawn into the steam injectors and discharged together with the steam through nozzles, against baffles. The lye is thus atomized and a high degree of concentration is obtained.

German Patent 282950 (1912).
Norwegian Patent 24561 (1913).
J. Soc. Chem. Ind. vol. 34 (1915) p. 656.
Chem. Abs. vol. 9 (1915) p. 2590.
Wochbl. Papierfabr. vol. 46 (1915) p. 1178.
Papier-Fabr. vol. 13 (1915) p. 314.
Papir J. vol. 2 (1914) p. 185.

Murbe, E.—EVAPORATION OF WASTE LIQUORS, ESPECIALLY SULPHITE AND SULPHATE LIQUORS.

The liquor is sprayed under pressure into a chamber in which it comes in direct contact with hot waste gases from the boiler furnace. Further concentration is effected in the usual way in separate evaporating chambers.

German Patent 293394 (1914).
J. Soc. Chem. Ind. vol. 35 (1916) p. 1106.

SOME MODERN EVAPORATORS.

The Kestner climbing film evaporator, the Soderlund and Boberg evaporator, and the Proche and Boillon "thermo-compressor" are described. A very high efficiency is claimed for the Soderlund and Boberg evaporator in virtue of the fact that the difference in temperature between the boiling liquid and the heating steam is very small (from 1° to 3° C.) A plant on this system is being erected in Sweden for treating waste liquors from wood-pulp manufacture.

J. Soc. Chem. Ind. vol. 36 (1917) p. 70.

Krause, G. A.—VAPORIZING OR CONCENTRATING LIQUIDS, SOLUTIONS, EMULSIONS, SUSPENSIONS, ETC.

The finely divided substance is injected upwords into a vertical cylindrical chamber, from a nozzle. A heated, gaseous drying-medium is injected tangentially at the bottom of the chamber so as to pass upwards to the outlet in a spiral path of uniform diameter around the jet of substance to be desiccated.

United States Patent 1213887 (1917).
J. Soc. Chem. Ind. vol. 36 (1917) p. 329.

Murbe, E.—PROCESS FOR THE EVAPORATION OF WASTE SULPHITE AND SULPHATE LIQUORS.

The waste liquors are sprayed in contact with furnace gases with simultaneous admission of air, the temperature of the mixing chamber and of the saturated flue-gases being maintained above the boiling point of water, preferably at 110°-120°C. A fan is arranged for the introduction of air into the lower portion of the mixing chamber and a drying arrangement is provided beneath the mixing chamber to receive the aqueous lignin liquor discharged from the bottom of the mixing chamber.

German Patent 297440 (1914).
Addition to German Patent 293394.
J. Soc. Chem. Ind. vol. 36 (1917) p. 870.

EVAPORATOR FOR WASTE LIQUOR.

A new evaporator, invented by Soderlund and Boberg, is described. The principle of the usual multiple-effect evaporators is the use of the steam formed in one evaporator for the liquor in the second evaporator. Hereby at least one-third or one-fourth of the steam is lost. With the new evaporator all steam or heat is utilized by increasing the temperature of the steam formed by the evaporation and using this warm steam for evaporation of further volumes of liquor. The increase in temperature is effected by a slight compression of steam. The new evaporator is put on the market by Aktiebolaget Industare, Gothenburg, 5, Sweden.

Svensk Pap. Tid. (1917) p. 22.
Papir. J. vol. 5 (1917) p. 92.
Pulp Paper Mag. Can. vol. 15 (1917) p. 445.

Landmark, H. B.—METHOD AND APPARATUS FOR RECOVERY OF FREE SO_2 FROM WASTE SULPHITE LIQUOR, WITH SIMULTANEOUS CONCENTRATION OF THIS BY MEANS OF ITS LATENT HEAT.

The liquor is atomized in an atomizer at its own pressure, whereby the SO_2 gas is removed. The liquor is afterwards passed into a container which is kept under strong vacuum in order to effect a high concentration by means of the latent heat of the liquor.

Norwegian Patent 28147 (1917).
Papir. J. vol. 5 (1917) p. 173.

MISCELLANEOUS

Zawadski and Meyer.—PROCESS FOR PRODUCTION OF VOLATILE DISTILLATION PRODUCTS FROM WASTE LIQUORS.

Claims: Process for production of wood alcohol, acetone, and other distillation products of wood from the waste liquors. The liquors concentrated as far as possible are made into a paste with charcoal, pressed into briquettes, and subjected to dry distillation. The free acid is removed, precipitated with sodium sulphate. Dry distillation of the residue is obtained by evaporation in mixture with charcoal.

German Patent 45951 (1888).
Austrian Privilegium 1210 (1889).
Ber. vol. 22 (1889) p. 75.

Nettl, A. S.—PROCESS FOR PREPARATION OF OXALIC ACID FROM SULPHITE LIQUOR.

The liquor filtered from mechanical impurities is treated with sulphuric acid and warmed to drive off all the SO_2. At the same time the lime is precipitated as $CaSO_4$. The H_2SO_4 is neutralized with $CaCO_3$ and the liquor is freed from the resulting $CaSO_4$ by filtration. The liquor is evaporated to 40° Bé., and finally to dryness, and is then mixed with 2 parts of caustic potash and 1 part of caustic soda. The mixture is heated in cast-iron vessels from 1 to 4 hours, above 180° C., avoiding carbonization. The mixture is then extracted for oxalic acid. Or the sulphite liquor freed from lime salts is concentrated to 30° Bé., and then mixed with sawdust and worked up to a thick paste which is then decomposed with caustic potash.

German Patent 52491 (1889).
Ber. vol. 24 (1891) p. 102.

Mitscherlich, A.—INNOVATIONS IN THE PROCESS OF PRODUCING TANNING MATERIALS WITH THE PRODUCTION OF THE BY-PRODUCTS CELLULOSE, GUMS, ACETIC ACID, AND CALCIUM BISULPHITE.

German Patent 4179.
(See "Tanning Materials" p. 78.)

Mitscherlich, A.—COOKING OF WOOD WITH CALCIUM BISULPHITE. RECOVERING CELLULOSE, TANNING MATERIALS, GUMS AND ACETIC ACID.

English Patent 1668 (1882).
(See "Tanning Materials" p. 78.)

Hartmann.—LIGNOSULPHITE.

The new treatment for pulmonary diseases by inhaling sulphite liquor vapours.

Papier-Ztg. vol. 20 (1895) pp. 822, 952, 1084, vol. 21 (1896) p. 764, vol. 24 (1899) p. 1667.

SULPHITE VAPOURS FROM THE SPENT LIQUORS OF WOOD-PULP MILLS AS A REMEDY FOR PULMONARY DISEASES.

An establishment has been opened at Hallein (Austria) for the treatment of patients suffering from lung and bronchial disorders by inhalation of "lignosulphite" as proposed by Dr. Hartmann. In the address at the opening of the institute Dr. Kellner said that "lignosulphite" was the name given to the lignin compound of the sulphurous acid. For the production of suitable compounds for inhalation, the digestion of the wood is conducted in a particular manner so as to obtain a considerable quantity of the volatile derivatives. For lung diseases, air is inhaled containing 0·003 per cent by volume of these volatile compounds (the compounds of the ethers of camphene and terebene with sulphurous acid being specially mentioned), the result of which is a distinct change in the bacillus expectorated.

It is well known that a small quantity of sulphurous acid in the atmosphere kills coniferous trees, and the ash obtained by burning the foliage of trees thus destroyed contains a considerable quantity of sulphurous acid. It has been shown that these plants possess the power of taking in, through the "stoma" of the epidermis, sulphurous acid which is oxidized to sulphuric acid and accumulates until it destroys the plant. The action of the sulphurous acid in the serum of the blood is somewhat similar to that in the plants, and owing to the large surface of the bronchial tubes of the lungs, the compounds of lignin and sulphurous acid are readily brought into contact with the blood, and absorbed. Tubercular laryngeal abscesses have been cured by a similar inhalation of antiseptic air.

Papier-Ztg. vol. 19 (1894) p. 2779.
J. Soc. Chem. Ind. vol. 14 (1895) p. 57.

Remy, P.—UTILIZATION OF SULPHITE LYE AS A WATERPROOFING SOLUTION FOR PAPER.

The liquor is treated with iron or lead salts in quantities equal to the calcium salts present, whereby a waterproofing solution is obtained. The iron salts are the more suitable, as lead salts are poisonous and also discolour the paper. The solution contains salts of other metals which may be removed before the treatment, and the lye may be evaporated before treatment to remove some of the SO_2. Examples of treatment of the liquor are given.

German Patent 90798.
Papier-Ztg. vol. 22 (1897) p. 426.
J. Soc. Chem. Ind. vol. 16 (1897) p. 630.

Schmidt, H.—PREPARATION OF ARTIFICIAL WOOD FROM WOOD AND WASTE LIQUOR.

Wood, sawdust, etc., are mixed with liquor that has been evaporated and treated with glue. The mixture is subjected to high pressure. The resulting product is preferable to wood in being lighter and in not swelling.

German Patent 86542 (1895.)
Ber. vol. 29 (1896) p. 452.

Hofmann, C.—KELLNER'S SULPHITE AND ELECTRIC PROCESS.

The author discusses Hartmann's "lignosulphite", the method of preparation of which is secret. It may be formed from sulphonated-lignin compounds with aromatic substances and combined with sulphurous acid.

Papier-Ztg. vol. 21 (1896) part II p. 2483.

WASTE SULPHITE LYE AND COMMON SALT.

As in most countries salt is taxed for manufacturing purposes whilst farmers who use it as a cattle food are exempt from the tax, a method of rendering the common salt unfit for manufacturing purposes but fit for cattle food is very much required. An addition of 5 to 10 per cent of waste sulphite lye is found to answer this purpose, being very difficult to remove from the salt and not rendering it distasteful to the cattle.

Papier-Ztg. vol. 23 (1898) p. 951.
J. Soc. Chem. Ind. vol. 17 (1898) p. 485.

Mullner, F.—PROCESS FOR REGENERATION OF ALKALI OF SULPHITE AND SULPHATE PROCESSES BY ALUMINA.

The partially evaporated liquor is treated with alumina and with a quantity of lime equivalent to the sulphur content, to prevent formation of sulphides of the alkalies. The mass is decomposed and calcined. The alkalies form aluminates which are treated with either CO_2 or SO_2.

German Patent 96467 (1897).
Chem. Zentr. (1897) part I p. 1183.
Papier-Ztg. vol. 23 (1898) pp. 687, 1062, 1218.
J. Soc. Chem. Ind. vol. 17 (1898) p. 688.

Pollacsek, E.—PROCESS FOR PURIFICATION AND UTILIZATION OF WASTE EFFLUENTS FROM SULPHITE MILLS.

Oxidation with air and ferric chloride, iron precipitated with caustic lime, and filtrate made acid. Recovery of gypsum from filtrate. A plastic mass of basic ironstone is obtained if pyrites residues or iron ore are added to the filtrate.

Austrian Privilegium 967 (1898).

Pollacsek, E.—PROCESS FOR RECOVERING VANILLIN FROM WASTE SULPHITE LIQUOR.

The liquor is treated with air and iron chloride, precipitated with caustic lime, and afterwards with sulphuric acid.

To the filtrate, sodium hydroxide or another alkali is added, and the precipitate, containing vanillin, is dissolved in hydrochloric acid. The vanillin is shaken out with ether or other solvent.

Austrian Privilegium 1524 (1898) and Austrian Privilegium 967.

Drewsen, V. and Dorenfeldt, L. J.—UTILIZATION OF WASTE SULPHITE LIQUORS.

Recovery of inorganic substances by treating the lye with lime in closed vessels and then treating the precipitate with sulphurous acid.

United States Patent 620751 and 620775 (1899).
Chem.-Ztg. vol. 23 (1899) p. 276.

Gawalowski, A.—WASTE SULPHITE LIQUOR AS DISINFECTING MATERIAL.

Papier-Ztg. vol. 24 (1899) p. 3112.
Chem. Tech. Ztg. (1899).

Bache-Wiig, B.—PRESERVATION OF FOODSTUFFS, PARTICULARLY EGGS.

The eggs are given a protective coating, which can be easily washed off, by dipping in concentrated sulphite liquor.

German Patent 129326 (1901).
Chem. Zentr. (1902) part I p. 740.

Koppert, K., Kammerer, F. J. F., Chem. Fabr.—PREPARATION OF BLACKING BY THE USE OF SULPHITE LIQUOR.

In place of crude glycerol, glue, gums, and molasses, thickened sulphite liquor is used to prepare acid-free blackings with the usual constituents.

German Patent 114401 (1899).
Chem. Zentr. (1900) part II p. 1046.

Drewsen, V. and Dorenfeldt, L. J.—PROCESS OF UTILIZING SULPHITE LYES.

The waste liquor of sulphite mills, containing sulphonates, is neutralized with liquor from the soda pulp, containing sodium sulphite, and the mixture is concentrated and calcined. The product is lixiviated and the solution is treated with lime, the soluble salts being drained off for further use.

United States Patent 726036 (1903).
J. Soc. Chem. Ind. vol. 22 (1903) p. 627.

UTILIZATION OF WASTE SULPHITE LIQUOR.

Drewsen and Dorenfeldt's process of mixing the waste liquor with recovered soda, and concentrating, has one drawback, namely that even with an excess of alkali during the concentration process aldehydes are formed which with the hot steam form alcohols and acid. This is not the case when the soda is replaced by waste liquor from a soda-pulp mill. The loss of about 10 per cent which is experienced in the recovery plant of soda mills is also eliminated by this method.

The process is as follows: 1. Neutralization by mixing sulphite and soda liquor; 2. Concentration of the neutralized liquor; 3. Fusing of the concentrated liquor; 4. Leaching of the residue; 5. Treatment of the solution with quicklime for the preparation of soda-cooking liquor.

Wochbl. Papierfabr. vol. 34 (1903) p. 2261.

Morterud, E.—PROCESS FOR OBTAINING GAS AND HEAT IN THE MANUFACTURE OF SULPHITE PULP.

The waste liquor (together with the pulp) is placed in an air-tight container under reduced pressure, whereby gas and excess heat is removed. The steam is condensed and the gas absorbed, or recovered, in other ways.

German Patent 180168 (1905).
United States Patent 833936 (1906).
Austrian Patent Application 6383 (1905).
Chem. Abs. vol. 1 (1907) p. 2204.
Wochbl. Papierfabr. vol. 38 (1907) p. 1056.
Papier-Ztg. vol. 31 (1906) part II p. 3819 vol. 32 (1907) part I p. 296.

Kumpfmiller, A.—PROCESS FOR PURIFICATION OF WASTE SULPHITE LIQUOR.

Recovery of an adhesive, binding, tanning, and filling material. The sulphurous acid is removed at high temperature. The calcium is precipitated by the addition of an acid. One modification of the process is to spray the hot liquor continuously or intermittently into a container under high vacuum.

Austrian Patent 40657 (1906).

Tillberg, E. W.—PROCESS FOR OBTAINING TANNINS, ALCOHOL, AND CELLULOSE FROM WOOD.

Swedish Patent 25283 (1907).

Trainer, E.—UTILIZATION OF WASTE SULPHITE LIQUOR.

Low-grade coal is mixed with waste liquor, the water evaporated, and the briquettes obtained by pressing are subjected to dry distillation. Combustible gases and fuel material are obtained.

Papier-Fabr. (1907) p. 641.
Papier-Ztg. vol. 32 (1907) p. 994.
Chem. Zentr. (1907) part II p. 109.

Ellis, C.—WASTE SULPHITE LIQUOR DISINFECTANT.

Claim is made for a disinfectant composition comprising creosote of about 1·1 sp. gr. and concentrated waste sulphite-cellulose liquor of about 1·3 sp. gr., the latter being present in excess.

United States Patent 877414 (1908).
Chem.-Ztg. vol. 32 (1908) Rep. p. 111.
J. Soc. Chem. Ind. vol. 27 (1908) p. 177.

Trainer, E.—RENDERING ORGANIC CONSTITUENTS OF SULPHITE LIQUOR INSOLUBLE.

The waste lyes are concentrated to about 30°Bé. and then heated with acids, when, according to the nature of the acid and the temperature, gelatinization of the mass takes place more or less rapidly. The gelatinization proceeds more quickly if an aldehyde be added to the lye before the treatment with acid. After treatment with formaldehyde and concentrated hydrochloric acid, for example, the whole mass solidifies almost immediately on heating. The process may be carried out in a closed vessel under pressure. The product may be used for the preparation of insulating materials, artificial leather, etc.

German Patent 197195 (1906).
Austrian Patent 36847 (1908).
J. Soc. Chem. Ind. vol. 27 (1908) p. 708.
Chem. Zentr. (1908) part I p. 1595.
Papier-Ztg. vol. 33 (1908) part I p. 1516.
Z. angew. Chem. vol. 21 (1908) p. 2539.
Chem. Abs. vol. 2 (1908) p. 2301.

Trainer, E.—RENDERING THE ORGANIC CONSTITUENTS OF WASTE SULPHITE LIQUORS INSOLUBLE.

The product obtained by treatment according to German Patent 197195 is dehydrated and heated to above 100°C. It can also be used as a decolorizing substance.

German Patent 202132 (1907).
Addition to German Patent 197195.
Chem. Zentr. (1908) part II p. 1389.
Wochbl. Papierfabr. vol. 39 (1908) p. 3238.
J. Soc. Chem. Ind. vol. 27 (1908) p. 1173.
Chem. Abs. vol. 3 (1909) p. 491.

Hough, W. J.—

Precipitation of resin from the liquor and the use of this material for the preparation of soaps and oils. Evaporation of liquor and destructive distillation of the lignin for obtaining gas and oil.

United States Patent 931608.
Papier-Ztg. vol. 34 (1909) p. 2787.
Pulp Paper Mag. Can. vol. 8 (1910) p. 48.

Diamond, B.—PREPARATION OF NEUTRAL SALT SOLUTIONS FOR WOOD PRESERVATION.

The liquor is neutralized with soda and then made strongly alkaline. The precipitate produced is filtered off. In the filtrate, iron vitriol, aluminium sulphate, and sodium fluoride are dissolved in the proportions of 6:1:1. No precipitate is produced. The resulting solution can be used to impregnate wood.

German Patent 216798 (1907) Cf. United States Patent 938128.
Chem.-Ztg. Rep. vol. 33 (1909) pp. 607, 624.
Jahrb. Chem. Techn (1909) part I p. 492.

Kirchner, E.—DAS PAPIER.

Das Papier, vol. 2, parts B and C.
(See " Effluents " p. 35.)

Melhardt, C.—CONVERSION OF PEAT LIGNITE INTO CHARCOAL.

Sulphite liquors which have been concentrated to a certain degree are non-hygroscopic, i. e. they will not absorb moisture from the air, but if mixed with substances containing water the concentrated liquor will take up the water, becoming more dilute thereby. By mixing peat with sulphite liquor the water of the peat is extracted, and after standing a short time the dehydrated peat after separation from the liquor may be used to make charcoal.

German Patent 148275 (1903).
Papier-Ztg. vol. 29 (1904) part I p. 574.
Jahrb. Chem. Techn. (1904) part I p. 6.

UTILIZATION OF LIQUOR.

The liquor, after addition of clay, may be used as a cementing material in the brick walls of kettles.

Deut. Techn. Ztg. vol. 20 (1903) p. 274.

Spatz, H.—PREPARATION OF FIREPROOF BRICK.

To highly silicious substances such as quartz, sand, and kieselguhr, sulphite liquor is added as a cementing material.

German Patent 159377 (1903).
Jahrb. Chem. Techn. (1905) part I p. 379.
Papier-Ztg. vol. 30 (1905) p. 1054.

Bergerhoff, E.—PREPARATION OF HALF-STUFF.

A pulp suitable for wrapping paper may be made by boiling the wood with waste liquor with the addition of some fresh bisulphite.

German Patent 160151 (1903).
Biedermann. Tech. Chem. Jahrb. (1904) p. 558.
Chem. Zentr. (1905) part I p. 1576.

PAPER-MILL WASTE TURPENTINE.

Refers to work to be done in the engineering laboratories of the University of Wisconsin at Madison, Wisconsin, U.S.A., on waste products from pulp-mills. The attempt will be made to utilize the so-called "spruce turpentine" as a fuel for internal combustion engines. Tests on the oil show that fully 85 per cent is cymol. It is claimed that about 50 barrels per year are available from a 25-ton mill using slabs. A higher yield is claimed from sound timber.

Pulp Paper Mag. Can. vol. 7 (1909) p. 145.

Diamond, B.—RENDERING BARRELS TIGHT.

The interior of the barrel is treated with waste sulphite pulp liquor resulting from the manufacture of cellulose from wood. The liquor should have a specific gravity of from 25° to 35° Bé., and is previously mixed with treacle, starch-paste or water-glass.

English Patent 5206 (1909).
J. Soc. Chem. Ind. vol. 28 (1909) p. 1239.

Diamond B.—NEUTRALIZATION OF AQUEOUS SALT SOLUTIONS.

The process depends on the fact that liquors of the kind in question hinder the precipitation of salts. The solutions obtained can be used to impregnate wood as a protective agent.

German Patent 222193 (1909) (Addition to German Patent 216798).
United States Patent 940394 (1909).
Z. angew. Chem. (1910) p. 1390.

Badische Anilin und Soda Fabrik.—PROCESS FOR MAKING SUSPENSIONS OF INSOLUBLE DYES IN WATER.

The dyestuff is heated with sulphite liquor. In certain cases the dye assumes the colloidal condition.

Chem. Zentr. (1910) part I p. 1998.

Deutsche Saduyn Gesellschaft M.B.H.—MEANS OF MAKING AUTOMOBILE GASES ODOURLESS.

Produce salts of lignosulphonic acid by addition of sodium chloride to liquor at 80°-100°. One kilogramme (2·2 lb.) of the dried substance in 5 litres (1·1 gallons) of water produces a solution which absorbs acrolein and other gases with an unpleasant odour.

Wochbl. Papierfabr. vol. 41 (1910) p. 3847.

Matheus.—BEHAVIOUR OF SULPHITE LYES WITH MILK OF LIME.

If cold or hot sulphite waste lye be treated with milk of lime until neutralized, a precipitate is formed containing calcium sulphate, calcium sulphite, and calcium salts of organic acids. If more lime be added, the precipitate is increased and the liquid assumes a yellowish colour. On filtering the liquid and adding a further quantity of lime it is found that a considerable portion of the latter is dissolved. If the yellow lye be then heated or if more milk of lime be added a large quantity of yellow precipitate is suddenly produced and the entire mass forms a thick paste. The liquid portion can be separated by filtration and the precipitate then appears to be composed of very small crystals of the calcium salt or salts of one or several very similar organic compounds. The moist precipitate readily dissolves when acidified with sulphuric acid; when it is decomposed, calcium sulphate separates out and a yellow or brown solution remains. If this be poured slowly into sulphuric acid at 30° Bé. whilst stirring, each drop congeals at once into a flaky grey mass, so that a large quantity of an organic substance is obtained which can be filtered off from the excess of acid. This organic substance when oxidized by nitric acid yields large quantities of crystals of oxalic acid.

Papier-Fabr. vol. 9 (1911) p. 1407.
J. Soc. Chem. Ind. vol. 30 (1911) p. 1375.
Chem. Abs. vol. 6 (1912) p. 1365.
Pulp Paper Mag. Can. vol. 10 (1912) p. 53.
Paper vol. 6 (1912) No. 5 p. 16.

Matheus.—DECOLORIZING CHARCOAL FROM SULPHITE LYES.

The sulphite waste lyes, either fresh or freed from sulphur dioxide by boiling, are neutralized, preferably with milk of lime, in a suitable vessel. The liquor is then concentrated to a thick syrup, and this is further evaporated in flat vessels until it swells up and solidifies on cooling to a brittle and readily friable mass. The powdered product is heated next with exclusion of air to produce destructive distillation, and an extremely porous charcoal is obtained possessing good decolorizing properties and capable of serving as a substitute for bone charcoal. At the same time a distillate is obtained closely resembling the distillate from wood.

Papier-Fabr. vol. 9 (1911) p. 1435.
J. Soc. Chem. Ind. vol. 30 (1911) p. 1446.
Chem. Abs. vol. 6 (1912) p. 1365.

DeCew, J. A.—PROCESS FOR PRESERVING WOOD.

The product is obtained by treating a fibro-cellular body with waste sulphite liquor under the action of heat and pressure.

United States Patent 1010122 (1911).
J. Soc. Chem. Ind. vol. 31 (1912) p. 29.

Stutzer, A.—SULPHITE LYES AS A PREVENTIVE FOR FOOT-AND-MOUTH DISEASE.

The foot-and-mouth disease is one of which the propagation is stimulated by an alkaline condition of the stalls and bedding; as a preventive the spraying with a dilute mineral acid has met with a fair success. But the handling of those acids prior to dilution, by farm labourers, presents a certain amount of risk, so the author suggests that the waste lyes from sulphite wood-pulp mills might be tried with good effect. The lyes should be transported either in barrels or absorbed in sawdust. In the former case the farmer should make a heap of dry sand or earth and pour the lye in the centre, subsequently mixing well. The material impregnated with the sulphite lye should be spread daily over the stalls and yards inhabited by the animals; treatment should be commenced before the disease has actually broken out.

Papier-Ztg. vol. 36 (1911) p. 3738.
Wochbl. Papierfabr. vol. 42 (1911) p. 4956.
Chem. Abs. vol. 6 (1912) p. 1850.
J. Soc. Chem. Ind. vol. 31 (1912) p. 121.

Bergstrom, H.—VOLATILE OIL FROM SULPHITE DIGESTION.

The vapours condensed from the digesters in the manufacture of sulphite wood-pulp yield an aqueous distillate containing methyl alcohol, acetone, aldehyde, and traces of acetic and formic acids, together with a brown oil which floats on the surface. This oil was formerly supposed to consist entirely of cymene, but the author's investigations show that it is a complex mixture. Fractional distillation of the oil between the limits of 150° and 270°C. yielded 7 per cent of a fraction, boiling point 150°-160°C. having a specific gravity of 0.845 optically inactive; this fraction was identical with that boiling at 149°C. obtained from the sulphate cellulose oil; it contains no terpene and is probably an oxygenated compound. The main product, distilling between 160° and 190°C., amounted to 55 per cent of the original oil and consisted mainly of cymene. The fraction 190°-210°C., amounting to 17 per cent of the oil, showed the maximum specific gravity of 0.951 and $[\alpha]_D=1.95°$; it was a thick, pale yellow oil. The distillate coming over between 205° and 250°C. solidified in the condenser to a mass of white crystals of the composition, $C_{10}H_{18}O$. The fraction 190°-210°C. probably contained also an acid body of the terpene series. Above 250°C. a fraction having a specific gravity of 0.925 and a slight dextrorotatory power distilled over; this fraction contained a sesquiterpene.

Papier-Fabr. vol. 10 (1912) p. 359.
J. Soc. Chem. Ind. vol. 31 (1912) p. 381.
Chem. Abs. vol. 6 (1912) p. 2528.

Raschig, F.—UTILIZATION OF SULPHITE LIQUOR IN AMMONIUM-NITRATE EXPLOSIVES.

The use of the evaporation residue of waste lyes from the manufacture of sulphite cellulose as a combustible substance in ammonium-nitrate explosives is claimed. The lye may be evaporated and the dry residue mixed with powdered ammonium nitrate or ammonium nitrate may be dissolved in the lye and the latter then evaporated, preferably on heated rotating drums. The explosives thus obtained detonate readily with fulminate caps, and may be admixed with up to 30 per cent of an inert substance and yet be capable of detonating. The products containing an admixture of an inert substance are specially suitable as safety explosives for mines.

French Patent 447419 (1912).
J. Soc. Chem. Ind vol. 31 (1912) p. 845.

Raschig, F.—EXPLOSIVE FROM WASTE SULPHITE LIQUOR.

Potassium or sodium nitrate is mixed with the waste lyes coming from the manufacture of cellulose by the sulphite or soda process. The liquid then flows on to highly-heated revolving rollers whereby almost immediate evaporation to dryness is obtained without any separation of the ingredients of the mixture. The dry material when scraped from the rollers is immediately ready for use and can be pressed in the dry state. The following are given as examples of this explosive: (1) Sodium nitrate (68 per cent), dry matter from either sulphite or soda-cellulose waste lyes (32 per cent). (2) Potassium nitrate (70 per cent), dry matter from sulphite-cellulose waste lyes (30 per cent).

English Patents 29696, 2069 (1912), Addition to English Patent 11568 (1912).
See French Patents 447419, 44149 (1912).
United States Patents 1056366 and 1056367 (1913).
J. Soc. Chem. Ind. vol. 32 (1913) p. 454.

Bergstrom, H. O. V. and Lindquist, B. O.—PURIFICATION OF LIQUID RESIN OBTAINED IN THE MANUFACTURE OF SULPHITE PULP.

The liquid resin is subjected to a distillation in vacuo at a temperature not exceeding 230°-250°C. with a view to destroying the lignin and similar compounds. The malodorous compounds go over first, the distillate being further purified with sulphuric acid, with passage of air if necessary.

Swedish Patent 33333 (1910).
Chem. Abs. vol. 7 (1913) p. 1288.

Sandberg, E. S. and Sundblad, G. K.—DESTRUCTIVE DISTILLATION OF ORGANIC MATTER IN WASTE LYES.

Waste lye from the manufacture of wood-pulp or other liquid containing organic matter is treated in two stages. The liquid is first spread in a thin layer on heated surfaces, whereby about 80 litres (17·6 gallons) of lye per minute are evaporated and the residue partially decomposed and carbonized, the carbon acting so as to remove adhesiveness. The solid residue then being easily and continuously removed by scrapers is passed through heated tubes by means of screw conveyors or is heated in ordinary retorts so as to be completely carbonized.

English Patent 24125 (1912).
J. Soc. Chem. Ind. vol. 32 (1913) p. 279.
Chem. Abs. vol. 8 (1914) p. 1346.

LIGNOSULPHITE INHALABORIUM.

An inhalaborium for lignosulphite is in continuous operation in Soolbad Frankenhausen.

Muller, Literatur der Sulfitablauge 1914 p. 30.

Muller, P. G.—PREPARATION OF AN ELASTIC MASS FROM WASTE SULPHITE LIQUOR.

Belgian Patent 255636 (1913).

Robeson, J. S.—PLASTIC MASSES FROM WASTE SULPHITE LIQUOR.

From concentrated liquor and clays.

United States Patent 1069031 (1913).
J. Soc. Chem. Ind. vol. 32 (1913) p. 864.

Platsch, M.—PRECIPITATION OF THE OBJECTIONABLE CONSTITUENTS OF WASTE SULPHITE LYES BY MEANS OF REAGENTS AFTER CONCENTRATION OF THE LYE.

The precipitation of the calcium salts as sulphate can be completely effected only after elimination of the volatile organic acids (acetic acid) by evaporation of the lyes to a syrupy consistency. The reagents then used must be such that their bases form with sulphurous acid only readily decomposable compounds or else do not combine at all. Aluminium sulphate, for instance, would be suitable, but precipitation may equally well be effected by sulphuric acid, provided the liquor be neutralized after the separation of the precipitate of calcium sulphate.

French Patent 447578 (1912).
United States Patent 1054141 (1913).
English Patent 19600 (1912).
J. Soc. Chem. Ind. vol. 32 (1913) pp. 284, 823.
Chem. Abs. vol. 7 (1913) p. 1415.

Ferenczi, S.—USE OF SULPHITE LIQUOR IN FOOT-AND-MOUTH DISEASE.

Sulphite liquor which had been made alkaline with NaOH was run into a stream. Cattle drinking from this stream were free from foot-and-mouth disease.

J. Landw. vol. 60 p. 183.
Z. angew. Chem. vol. 25 (1912) p. 2088.

Baekeland, L. H.—IMPREGNATING WOOD WITH SULPHITE LIQUOR.

A "fibrocellular body" is treated with waste sulphite liquor under the action of heat and pressure.

United States Patent 1057211 (1913).
J. Soc. Chem. Ind. vol. 32 (1913) p. 427.

Baekeland, L. H.—IMPREGNATED WOOD.

The pores of the wood are impregnated with mineral salts $ZnCl_2$ with or without water-glass and with the solid constituents of sulphite waste liquor.

United States Patent 1057319 (1913).
J. Soc. Chem. Ind. vol. 32 (1913) p. 428.
Chem. Abs. vol. 7 (1913) p. 1796.
Paper Trade J. vol. 57 (1913) No. 20 p. 46.

Rinman, E. L.—APPARATUS FOR DESTRUCTIVE DISTILLATION OF SULPHITE LYES.

Distillation is effected in an annular furnace in which an annular hearth is mounted. The material is distributed over the hearth and heating gases are passed through an annular space below the hearth, the latter being rotated in the opposite direction to the flow of the heating gases. The heating chamber is closed against the space above the hearth by liquid or sand-seal, and the conduit through which the distillation residue is discharged is connected with a vertical pipe of such height that the column of residue therein is sufficient to provide a gas-tight seal.

German Patent 269994 (1913).
J. Soc. Chem. Ind. vol. 33 (1914) p. 346.

Coughlin, M. F.—COMPOSITION FOR VARNISH, CONTAINING WASTE SULPHITE LIQUOR AND SHELLAC.

The composition consists of an ammoniacal solution of shellac together with the solid constituents of waste sulphite liquor.

United States Patent 1103267 (1914).
J. Soc. Chem. Ind. vol. 33 (1914) p. 931.

Lederer, A. and E.—RECOVERY OF VOLATILE ACIDS, ETC. FROM HYDROLYSIS OF LIGNOCELLULOSES.

The volatile products formed in the hydrolysis of lignocelluloses are removed by distillation under pressure from the mass in course of hydrolysis. The condensed liquid is fractionated by subsequent distillation, volatile acids, furfural, methyl alcohol, and acetone being obtained. The volatile products still remaining in the hydrolysed mass are separated by drying the latter in vacuo at not above 80°C. until it contains only 5-10 per cent of moisture. No destruction of sugar takes place at this temperature, but if a higher temperature be desired calcium acetate may be added to neutralize the mineral acid present.

French Patent 464608 (1913).
J. Soc. Chem. Ind. vol. 33 (1914) p. 478.

Meunier, L.—USE OF SULPHITE-CELLULOSE EXTRACTS FOR VARNISH.

A varnish giving rapidly drying, uniform coatings is prepared by mixing commercial concentrated sulphite-cellulose extract with a substance, especially a solution of a terpene in a sulphoricinate, which diminishes the surface tension of the product. For example, 4 litres (0.88 gallons) of oil of turpentine are added gradually, with constant agitation, to 25 kilogrammes (55 lb.) of neutral sodium sulphoricinate heated to 60°C., and the resulting thick liquid is incorporated with 25 times its weight of sulphite-cellulose extract of 30°Bé. (specific gravity 1.263).

French Patent 466196 (1913).
J. Soc. Chem. Ind. vol. 33 (1914) p. 604.

Ekstrom, G.—REMOVAL OF ORGANIC CONSTITUENTS FROM SULPHITE LIQUORS AFTER FERMENTATION.

Alcohol is first produced from the lye in the usual manner and the residual lye treated with a basic reagent, e.g. caustic lime, and then oxidized by aeration. Humus-like calcium compounds are precipitated; alternatively, aeration may be performed in the presence of an oxidizing catalyser.

United States Patent 1087356 (1914).
Chem.-Ztg. vol. 38 (1914) p. 25.
J. Soc. Chem. Ind. vol. 33 (1914) p. 349.
Chem. Abs. vol. 8 (1914) p. 1346.

Grothe, O.—PROCESS FOR TREATING SULPHITE LIQUOR.

The neutral liquid, after the removal of the free sulphurous acid, is concentrated and the sulphur-bearing groups of the organic compounds are removed by subjecting the liquor to the action of a cyanide or cyanamide compound under heat and pressure.

The product of the reaction is diluted with water and an organic cyanogen or cyanamide compound precipitated by a mineral acid; the precipitate is filtered off and dried at the ordinary temperature and used for tannin.

United States Patent 1087911 (1911).
J. Soc. Chem. Ind. vol. 33 (1914) p. 349.

Coughlin, M. F. and Sweet, C. E.—PROCESS OF BLEACHING SULPHITE LIQUOR.

The waste sulphite liquor is first treated with an oxidizing agent (permanganate) and then with a reducing agent (hydrosulphite).

United States Patent 1114120 (1914).
J. Soc. Chem. Ind. vol. 33 (1914) p. 1152.
Chem. Abs. vol. 8 (1914) p. 3858.
Paper vol. 15 (1914) No. 7 pp. 24, 32.

Coughlin, M. F. and Sweet, C. E.—PREPARATION OF A FINISHING COMPOSITION.

A waxy material, with or without a soluble soap, is incorporated with waste sulphite liquor in such proportion as to be readily emulsified with water.

United States Patent 1114119 (1914).
J. Soc. Chem. Ind. vol. 33 (1914) p. 1153.

Coughlin, M. F.—VARNISH CONTAINING SULPHITE LYE AND SHELLAC.

The composition consists of an ammoniacal solution of shellac together with the solid constituents of waste sulphite liquor.

United States Patent 1103267 (1914).
J. Soc. Chem. Ind. vol. 33 (1914) p. 931.

Bantlin, G.—PYROGENIC DECOMPOSITION OF WASTE SULPHITE LIQUOR.

Methyl alcohol is not formed, but large quantities of hydrogen disulphide and mercaptans are produced. The coking of the liquor therefore seems economically impossible.

J. Gasbel. vol. 57 (1914) p. 32.
Chem. Zentr. (1914) part I p. 923.
Chem. Abs. vol. 8 (1914) p. 1344.

Rinman, E. L.—UTILIZATION OF WASTE SULPHITE LIQUOR.

The organic substances in the waste sulphite liquor can be transformed into the same products as are formed in the soda or sulphate process by a special treatment with lime at high temperature. By dry distillation, acetone spirit, light and heavy oils, and combustible gases are obtained. Also SO_2 recovered in form of $CaSO_3$. Sawdust, etc., may be added to the liquor with advantage. Description of process and results obtained are given. Five cubic metres (220 gallons) of sulphite lye from one metric ton (2,204 lb.) of pulp, yield: 125 kilogrammes (275 lb.) calcium sulphate; 250 kilogrammes (550 lb.) humic substances; 16·5 kilogrammes (36·3 lb.) acetone spirit; 15 kilogrammes (33 lb.) light oils; 10 kilogrammes (22 lb.) heavy oils. If sawdust is added to the lye the yield is higher.

Rep. Assoc. German Pulp and Paper Chemists (1914).
Wochbl. Papierfabr. vol. 46 (1915) p. 990.
Chem.-Ztg. vol. 39 (1915) p. 99.
J. Soc. Chem. Ind. vol. 34 (1915) p. 274.
Papier-Ztg. vol. 40 (1915) pp. 559, 574.
Chem. Abs. vol. 9 (1915) p. 2709.
Paper vol. 16 (1915) No. 9 p 11.
Pulp Paper Mag. Can. vol. 13 (1915) p. 337.

Gunther, W.—STABILIZING SULPHITE LYE.

In stabilizing sulphite lyes used for water purification, the disadvantages resulting from the varying composition of the concentrated lyes is overcome by evaporating them at the lowest possible temperature to dryness so that the organic matter will not be destroyed and by combining the free alkali at the same time or subsequently with CO_2 (air combustion gases).

French Patent 457159 (1913).
Chem. Abs. vol. 8 (1914) p. 2018.

Muller, M.—NEW SUGGESTIONS WITH REGARD TO EVAPORATION AND TREATMENT OF INDUSTRIAL WASTE WATERS.

Wochbl. Papierfabr. Annual number (1914) p. 2276.

Oman, E.—PROCESS FOR MANUFACTURING SULPHITE PULP.

Waste liquor is used instead of water for preparation of cooking liquor by dissolving lime and sulphurous acid. When the liquor after several "cooks" has reached a certain concentration of organic matters it is worked up for by-products.

French Patent 467466 (1914).
English Patent 1145 (1914).
Canadian Patent 154165 (1914).
United States Patent 1130192 (1915).
J. Soc. Chem. Ind. vol. 33 (1914) p. 348, vol. 34 (1915) p. 419.
Chem. Abs. vol. 8 (1914) p. 2805, vol. 9 (1915) pp. 1319, 1843.
Pulp Paper Mag. Can. vol. 12 (1914) p. 282.
Paper vol. 14 (1914) No. 8 p. 20 also vol. 16 (1915) No. 6 p. 19.

Aktieselskabet Sulfitsprit.—PROCESS FOR OBTAINING ORGANIC SUBSTANCES FROM WASTE SULPHITE LIQUOR.

The remaining liquor after the alcohol has been distilled off is mixed with sulphuric acid containing wash water from the washing of the SO_2 gases and boiled at a pressure of less than 12 atmospheres.

Norwegian Patent 25927 (1915).
Papir J. vol. 3 (1915) No. 15 p. 190.

Platsch, M.—PROCESS FOR PURIFICATION OF CONCENTRATED WASTE SULPHITE LIQUOR BY PRECIPITATING THE LIME WITH SULPHURIC ACID.

Sulphuric acid is added to the cold liquor in such a quantity as to precipitate all the lime. Traces of sulphuric acid are afterwards removed by the addition of a base.

Norwegian Patent 26028 (1915).
Papir J. vol. 3 (1915) No. 15 p. 203.

Schmidt, A.—A NON-EXPLOSIVE FUNGICIDE.

United States Patent 1136723 (1915).
Chem. Abs. vol. 9 (1915) p. 1526.

DeCew, J. A.—PROCESS FOR PRESERVING AND HARDENING OF WOOD AND THE LIKE AND FOR RENDERING WOOD AND WOOD PRODUCTS FIREPROOF.

Creosote oil or crude petroleum is emulsified with the waste sulphite liquor, and the emulsion is used for impregnating the wood after the addition of magnesium chloride, mercury chloride or copper sulphate.

Norwegian Patent 26293 (1915).
United States Patent 1155708 (1915).
Papir J. vol. 3 (1915) p. 262.
J. Soc. Chem. Ind. vol. 34 (1915) p. 1244.
Paper-Maker Brit. Trade J. vol. 49 (1915) p. 332.

Hedden, M. W.—PROCESS OF TREATING WASTE SULPHITE LIQUOR.

Neutralized waste sulphite liquor is digested with a cyanogen compound to remove all the sulphur-bearing groups and then saturated with sodium chloride or an electrolyte, other than a mineral acid, to precipitate organic cyanogen compounds.

United States Patent 1130817 (1915).
J. Soc. Chem. Ind. vol. 34 (1915) p. 419.
Chem. Abs. vol. 9 (1915) p. 1115.

Knight, O. W.—PROCESS OF TREATING SULPHITE WASTE LIQUOR AND PRODUCT THEREOF.

A liquor containing a lignone derivative, e.g. fermented waste sulphite liquor, in which at least part of the alcohol has been oxidized to aldehyde, is treated with a phenolic substance in presence or absence of a condensing agent at a temperature sufficient to produce a condensation product.

United States Patent 1143714 (1915).
J. Soc. Chem. Ind. vol. 34 (1915) p. 830.
Paper Trade J. vol. 61 (1915) No. 3 p. 50.
Paper vol. 17 (1915) No. 2 p. 18.

Wegelin, A. Akt. Ges. f. Russfabrikation.—MANUFACTURE OF AN EXPLOSIVE FROM LIQUID AIR AND CARBON FROM WASTE SULPHITE CELLULOSE LYE.

Coke prepared by carbonization of waste sulphite liquor is impregnated with liquid air.

French Patent 474819 (1914).
J. Soc. Chem. Ind. vol. 34 (1915) p. 1119.

Bergstrom, H.—UTILIZATION OF VOLATILE WASTE PRODUCTS OF SULPHITE-CELLULOSE MANUFACTURE.

If the vapours "blown off" from the sulphite digesters be condensed, sulphurous acid, methyl alcohol, cymene, and small quantities of furfural and of a solid terpene alcohol can be recovered from the condensed liquid, which contains 100 grammes of sulphurous acid (1 lb. per gallon) and 5-5.5 grammes of methyl alcohol per litre (0.05-0.055 lb. per gallon), and 1-1.5 litres (0.22-0.33 gallons) of oil, furfural, etc. per metric ton (2204 lb.) of cellulose. Moreover, the quality of the cellulose would be improved by removing these products from the condensed liquid before using it again in the boiling process. Considerable quantities of methyl alcohol, and possibly also some acetic acid, could be recovered by evaporating the spirit lyes from the digesters.

Papier-Fabr. vol. 12 (1914) p. 1040.
Z. angew Chem. vol. 28 (1915) Rep. 47.
J. Soc. Chem. Ind. vol. 34 (1915) p. 487.
Chem. Abs. vol. 9 (1915) p. 149.
Chem. Trade J. vol. 57 (1915) p. 208.
Papir J. vol. 2 (1914) p. 389.

Fosse, H. W.—NORWEGIAN TURPENTINE OIL FROM SULPHITE-CELLULOSE MANUFACTURE.

The crude oil, obtained as a by-product in sulphite-cellulose manufacture, had a specific gravity at 15/15°C. of 0.8918 $\left[\alpha\right]^{20}_{D} = +7.8°$ and contained no free acids; the greater part boiled between 157° and 160°C. The oil contained sulphur compounds and oxygenated substances, and had an unpleasant odour. The sulphur compounds and unpleasant odour were largely removed by treatment with calcium hypochloride. The oil contains about 80 per cent of *d*-pinene, with small amounts of sylvestrene and sesquiterpenes.

Ber. Pharm. Ges. vol. 25 (1915) p. 303.
J. Soc. Chem. Ind. vol. 34 (1915) p. 1261.

Lorentz, K.—LIQUID SWEDISH RESIN FROM WOOD-PULP WASTE LIQUOR.

The resin from sulphite pulp waste lye has a high sulphur content and an unpleasant odour. It is soluble in water and has drying properties. It is not suitable for soap manufacture but may find application in the varnish industry, in the preparation of wagon grease, lubricants for driving belts, and bird lime. The crude resin may be refined by distillation by boiling with sulphuric acid or with a strong solution of sodium chloride and milk of lime, or by saponification.

Seifensieder-Ztg. vol. 43 (1916) pp. 400, 501.
Z. angew. Chem. vol. 29 (1916) Rep. p. 445.
J. Soc. Chem. Ind. vol. 35 (1916) p. 1163.

Freeman, W. K.—INSULATING MATERIAL, PLASTIC COMPOSITION, AND CEMENT COMPOSITION FROM WASTE SULPHITE LIQUOR.

The liquor is concentrated, treated with hydrochloric acid, agitated and boiled, partially cooled, treated with ammonia, agitated by beating so as to precipitate sulphur calcium compound in an inert form, allowed to settle, and the product evaporated. Partially evaporated lye may be treated with an alkali chloride, agitated while hot, partially cooled, and treated with barium chloride. The liquor treated in this way may be dried with the precipitate therein, mixed with an oxide and chloride capable of forming an oxychloride binding agent for insulating purposes. The liquor treated as above may be separated from the precipitates evaporated, dried and powdered, and mixed with a small quantity of gum camphor, with or without powdered, indurated, vegetable fibre, and then with a mixture of powdered metallic oxide and chloride adapted when wet to form an oxychloride binding agent. The liquor treated as above, dried without removing the precipitate, and powdered, is mixed with the powdered components of an oxychloride binding agent and with finely disintegrated wood which has previously been treated with an oxychloride cement, allowed to set, and then disintegrated.

United States Patent 1175422-1175426 (1916).
J. Soc. Chem. Ind. vol. 35 (1916) p. 533.
Chem. Abs. vol. 10 (1916) p. 1434.

Welsh, J.—SULPHITE LIQUOR FOR RE-PULPING NEWSPAPER.

The process of removing ink, colouring matter or pigments from waste papers by the use of spent digester liquids.

United States Patent 1175853.
Paper vol. 18 (1916) No. 2, p. 14.

Freeman, W. K.—PLASTIC COMPOSITION FROM WASTE SULPHITE LIQUOR.

Composition articles are made by mixing powdered "xylium" with powdered magnesium oxide and disintegrated fibrous material, moistening the mass with a solution containing magnesium chloride to form a plastic mass, the chloride being in sufficient quantity to form an oxychloride bond, and bringing the mass in contact with hot surfaces to remove excess moisture and press it into form.

United States Patent 1175427 (1916).
J. Soc. Chem. Ind. vol. 35 (1916) p. 534.

Beveridge, J.—THE UTILIZATION OF WASTE SULPHITE LYES.

The author mentions the various processes for utilization, especially the manufacture of tanning extracts. Finally the recovery of inorganic substances is discussed.

J. Soc. Chem. Ind. vol. 35 (1916) p. 563.
Paper vol. 18 (1916) No. 16, p. 17.
Chem. Abs. vol. 10 (1916) p. 2799.
(See "Tanning Materials" p. 78.)

Rinman, E. L.—PROCESS FOR TREATING WASTE SULPHITE LIQUORS WITH ALKALI.

Sulphite residues are boiled with alkalies, particularly calcium hydroxide, preferably under pressure, until they are transformed into a precipitate of lignin and calcium hydroxide, with or without superheated steam. Organic substances such as sawdust and bark may be added and the soluble product, especially if freed from calcium sulphite, may be made into briquettes for fuel, with or without admixture of other organic material. No mercaptans are formed in the dry distillation, provided that the boiling with lime has been continued long enough and at sufficiently high temperature. The distillate contains acetone, wood spirit, ethyl alcohol, ammonia and other nitrogenous compounds, and an oily mixture of higher alcohols, aldehydes, ketones, and hydrocarbons. By admitting sufficient air to the hot residue it may be burnt to lime, which is used again, and the heat developed may be used for another dry distillation. The waste lye may be freed from sulphurous acid before treatment and may also be previously fermented.

German Patent 285752 (1914).
United States Patent 1202317 (1916).
Swedish Patent 42108 (1917).
J. Soc. Chem. Ind. vol. 34 (1915) p. 1139, vol. 35 (1916) pp. 1010, 1215.
Chem. Abs. vol. 10 (1916) p. 1595 vol. 11 (1917) pp. 99, 2153.

Messow, H.—MANUFACTURE OF ARTIFICIAL GRAPHITE FROM WASTE LYES FROM CELLULOSE MANUFACTURE.

Waste lyes from the manufacture of cellulose are mixed with oxides of heavy metals, e.g. ferric oxide, and with calcium phosphate, and the mixture is exposed to high temperature and a very high pressure.

German Patent 297075 (1915).
J. Soc. Chem. Ind. vol. 36 (1917) p. 873.

Oman, E.—LIGNIN AND LIGNONE DERIVATIVES.

Lignin sulphonates and lignone sulphonates separated by saturating waste liquor with a salt such as Na, K, NH_4 chloride or sulphate; lignin sulphonates are precipitated, lignone sulphonates remain in solution. Oxylignin and oxylignon are obtained by treating the lignin or lignone sulphonates with alkali.

British Patent 106493 (1917).
Pulp Paper Mag. Can. vol. 15 (1917) p. 924.

Loffl, K.—SULPHITE LIQUOR FOR WASHING PURPOSES.

By making the liquor into a paste with infusorial earth or sand it could be used by the soldiers in the field for washing. The addition of ½ per cent Na_2CO_3 increases its detersive powers. By adding 2 per cent of crude cresol to the liquor it makes an excellent agent for killing body lice, and by incorporating 10 per cent of cresol it makes a good and cheap cleanser and disinfectant for floors.

Seifenseder-Ztg. vol. 42 (1915) p. 431.
Chem. Abs. vol. 10 (1916) p. 1443.

Rinman, E. L.—TREATMENT OF WASTE SULPHITE LIQUOR.

Treatment with caustic lime and destructive distillation of precipitate.

Norwegian Patent 26603 (1914).
Swedish Patent 42108 (1917).
Papir J. vol. 4 (1916) p. 47.
Chem. Abs. vol. 11 (1917) p. 2153.
Pulp Paper Mag. Can. vol. 15 (1917) p. 741.

Puring, J., Robeson Process Co.—WOOD STAIN FROM WASTE SULPHITE LIQUOR.

The stain consists of an emulsion of concentrated sulphite-cellulose waste liquor, linseed oil, and a little sulphuric acid, with or without the addition of formaldehyde.

United States Patent 1185604 (1916).
J. Soc. Chem. Ind. vol. 35 (1916) p. 747.
Chem. Abs. vol. 10 (1916) p. 1939.

Kertesq, Z.—VOLATILE ORGANIC COMPOUNDS, ESPECIALLY ESSENTIAL OILS FORMED IN THE SULPHITE PROCESS.

The liquor mixed with (1) powdered chalk, (2) ammonium sulphate, or (3) manganese sulphate aerated and fermented. The alcohol yields, including methyl alcohol, acetone, and acetaldehyde were: (1) 0·894 per cent, (2) 0·874 per cent, (3) 0·868 per cent.

From 1,000 litres (220 gallons) of liquor were separated, 0·06 kilogrammes (0·132 lb.) acetaldehyde, 0·2 kilogrammes (0·44 lb.) acetone, 0·53 kilogrammes (1·17 lb.) methyl alcohol, and 6·33 kilogrammes (13.9 lb.) ethyl alcohol. Further there were isolated a sesquiterpene $C_{15}H_{24}$ (B. p. 250°-260° C., sp. gr. 0·925) and a diterpene $C_{20}H_{32}$ (B. p. above 300° C., sp. gr. 0·950).

Chem.-Ztg. vol. 40 (1916) p. 945.
Chem. Abs. vol. 12 (1917) p. 1040.
Paper-Maker and Brit. Trade J. vol. 52 (1917) p. 36.
Pulp Paper Mag. Can. vol. 15 (1917) pp. 236, 306.
Paper Makers' Monthly J. vol. 55 (1917) p. 49.
Paper vol. 19 (1917) No. 17, p. 15.

Strehlenert, R. W.—HYDROLYSIS OF PEAT: STREHLENERT'S SULPHITE FUEL PROCESS.

About 75 per cent of the dry substances in the waste sulphite liquor are easily decomposed by Strehlenert's process. The remaining 25 per cent can only be decomposed at considerably higher temperatures and by the addition of larger quantities of sulphuric acid. In order to facilitate the removal of water from peat this is heated to 180° C. at 8 atmospheres pressure, whereby the humic acids present in peat serve as hydrolyzing agents. By using the liquor from the fuel process which contains 0·35 per cent sulphuric acid, of which 0·2 per cent is free acid, the hydrolysis can be effected at 140° C. and 6 atmospheres pressure within 20 minutes. At the same time the dry substance remaining in the liquor after the fuel process is precipitated in the peat. With a centrifuge, the peat can be dried to 25 per cent and by pressing after centrifuging to 50-55 per cent dry substance. The calorific value of the peat obtained in this was 5,260 calories at a moisture content of 6·4 per cent and an ash content of 3·6 per cent. Calculations show that at the same time one ton of sulphite fuel is produced 1,550 kilogrammes peat fuel can be obtained. The heat required for the production of peat fuel amounts to 20 per cent of the heat value produced.

Papir J. vol. 5 (1917) p. 101.
Pulp Paper Mag. Can. vol. 15 (1917) p. 764.

Enger, P. G.—APPARATUS FOR THE EXTRACTION OF HYDROCARBONS, ETC. ESPECIALLY CYMOL, IN THE MANUFACTURE OF SULPHITE PULP.

Several tanks are provided, one of them having an inlet connected with the top of the digester and an outlet near the top of the tank leading to an inlet near the bottom of the second tank. The second tank has an outlet near the bottom diametrically opposite the inlet, leading to an inlet in the third tank at a slightly higher level than the outlet in the second tank, and a return pipe is provided from the third tank to the digester.

United States Patent 1223158 (1917).
J. Soc. Chem. Ind. vol. 36 (1917) p. 593.
Chem. Abs. vol. 11 (1917) p. 1903.
Pulp Paper Mag. Can. vol. 15 (1917) p. 741.

Reed, H. C.—OXALIC ACID FROM WASTE PULP LYES.

The liquor is reduced to an approximately dry residue and concentrated nitric acid added in the proportion of 300 lb. of acid to 100 lb. of residue, the temperature being maintained at about 95°C. until oxidation is complete. Excess of nitric acid and water are then driven off by heat, and the oxalic acid is recovered by crystallization.

United States Patent 1217218 (1917).
J. Soc. Chem. Ind. vol. 36 (1917) p. 503.
Chem Abs. vol. 11 (1917) p. 1545.

Coughlin, M. F.—RUBBER COMPOSITION AND PROCESS FOR MAKING THE SAME.

Rubber is incorporated with dry sulphite waste lye solids, blown petroleum, and asphalt, with or without other loading materials.

United States Patent 1217157 (1917).
J. Soc. Chem. Ind. vol. 36 (1917) p. 512.

Knopflmocher, A.—CHARCOAL FROM WASTE SULPHITE LIQUOR.

Four thousand kilogrammes (8800 lb.) of waste liquor, 400 kilogrammes (880 lb.) of potassium carbonate, 38 kilogrammes (83·5 lb.) of calcium oxide, and 60 kilogrammes (132 lb.) of ground unburnt lime are evaporated to dryness and heated to redness in an iron vessel with the exclusion of air, the evolved gases being drawn off. The resulting material is treated in a Shanks lixiviating apparatus, and the residue extracted in a centrifuge or filter press. The calcium compound may be extracted with acids, e.g. hydrochloric acid, and the remaining charcoal dried and ground. The filtered potassium carbonate solution of about 25°Bé. (specific gravity 1·21) is mixed with about 30 kilogrammes (66 lb.) of potassium bicarbonate, evaporated to 50°Bé. (specific gravity 1·53) drawn off from the slight residue of potassium sulphate, and added to a fresh quantity of waste liquor for treatment as above. About 100 kilogrammes (220 lb.) of highly active decolorizing charcoal is obtained. To obtain charcoal free from ash a mixture of 4,000 kilogrammes (8,800 lb.) of waste liquor, 38 kilogrammes (83·5 lb.) of calcium oxide, and 100 kilogrammes (220 lb.) of unburnt lime is evaporated to dryness and the residue lixiviated with 645 litres (142 gallons) of potassium carbonate of density 45°Bé. (specific gravity 1·45) derived from the preceding operation. The mixture is filtered, dried, and heated to redness, and then treated as in the first example, with the omission of the acid treatment.

English Patent 102608 (1916).
Paper Makers' Monthly J. vol. 55 (1917) p. 259.
J. Soc. Chem. Ind. vol. 36 (1917) p. 589.

Oman, E.—LIGNIN AND LIGNONE DERIVATIVES.

Precipitation of lignin compounds, formation of nitro compounds, etc.

English Patent 103649-103655 (1917).
Chem. Abs. vol. 11 (1917) p. 1749.
Pulp Paper Mag. Can. vol. 15 (1917) p. 719.

GENERAL

Ekman, C. D.—WASTE SULPHITE LIQUOR.

A discussion of various methods of utilization.

See "Gums, Adhesives, and Sizing Materials" p. 68.)

POLLUTION OF RIVERS BY, AND UTILIZATION OF, WASTE SULPHITE LIQUOR (DISCUSSION).

Hofmann, C., Handbuch der Papierfabrikation (1897) 2nd edition pp. 1618, 1622.
Schubert: The Manufacture of Cellulose (1899) p. 174.
Griffin, R. B. and Little, A. D.: Chemistry of Paper-making, New York (1894) p. 270 and (1917) p. 270.

Seidel, H.—DEXTRONE.

According to Seidel, Ekman's Dextrone is impure lignosulphonic calcium. The most important quality of the dry residue of waste liquors is the reducing quality. From dinitronaphthalene a brown dyestuff can be obtained as well as from dextrose.

Third International Congress for Applied Chemistry, Vienna, 1898.

Harpf, H.—UTILIZATION OF WASTE SULPHITE LIQUOR.

Paper read before the third International Congress for Applied Chemistry, Vienna, 1898.

Z. angew. Chem. vol. 11 (1898) pp. 875, 925, 1169.
Chem. Zentr. (1899) p. 313.
(See "Composition" p. 12.)

Seidel, H. and Hanak, L.—WASTE SULPHITE LIQUOR.

(See "Composition" p. 12.)

Harpf, A.—UTILIZATION OF WASTE SULPHITE LIQUOR.

Z. angew. Chem. (1898) p. 925.
Jahrb. Chem. Techn. (1898) p. 114.
J. Soc. Chem. Ind. vol. 17 (1898) p. 1171.

Ferenczi, S.—RECOVERY OF WASTE FROM SULPHITE LIQUORS.

Papier-Ztg. vol. 22 (1897) pp. 3575, 3647, 3679.
J. Soc. Chem. Ind. vol. 17 (1898) p. 264.

Seidel, H.—WASTE SULPHITE LIQUOR.

Review of literature connected with the composition and utilization of the waste liquor.

(See "Composition" p. 12.)

Dorenfeldt, L. J.—WASTE SULPHITE LIQUOR.

A short notice explanatory of Seidel's comment (1900) on the Dorenfeldt-Drewsen process.

Z. angew. Chem. vol. 14 (1901) p. 82.

Gottstein, L.—THE PAPER PULPS FROM WOOD AND WASTE WATER FROM THE SAME.

Papier-Ztg. vol. 26 part I (1907) p. 828.
J. Soc. Chem. Ind. vol. 20 (1901) p. 495.

Fittica, F.—HISTORY OF THE MANUFACTURE OF SULPHITE PULP.

L. Hirzel, Leipzig (1902).
Papier-Ztg. vol. 27 (1902) part II p. 3144.

WASTE LIQUORS FROM CELLULOSE.

Discuss sulphite process, and general mention of utilization as adhesives, tannins, alcohol, tannin glue. Also includes discussion of waste liquors from soda process.

Pulp Paper Mag. Can. vol. 1 (1903) p. 80-82.

HOW STRAWBOARD FACTORIES KILL FISH.

Fish killed in White River, Indiana, U.S.A. by a sediment of gluey consistency which lodges in the gills.

Pulp Paper Mag. Can. vol. 2 (1904) p. 150.

Faust, A.—UTILIZATION OF WASTE LIQUOR FROM PULP-MILLS.

Manure, rosin, gum, tannin, alcohol.

Papier-Fabr. vol. 3 (1905) p. 785.

Gottstein, L.—ON THE PRODUCTION OF CELLULOSE FROM STRAW AND SUPHITE WASTE LIQUOR.

Remarks on R. Dietz's paper on same subject. Neither Dorenfeldt's nor Frank's process have been adopted in the pulp-mills. In the few cases where Frank's process was put into use it has in each case been given up. All the proposed uses take care of liquor from only a small fraction of the output. Refers briefly to Lindhardt's proposals.

Wochbl. Papierfabr. vol. 36 part I (1905) pp. 1390, 1616, 1779.
Z. angew. Chem. vol. 18 (1905) p. 983.

Lindhardt.—CONTRIBUTION OF THE IMPROVEMENTS OF COOKING LIQUORS AND UTILIZATION OF COOKING LIQUORS.

Zentr. oesterr-ungar. Papierind. (1905) p. 13.
Z. angew. Chem. vol. 18 (1905) p. 983.

UTILIZATION OF SULPHITE LIQUOR.

Conference of the Verein Deutscher Zellstoffabrikanten.—Behrend reported on the position of the sulphite liquor question in America. Gottstein stated that Knoesel-meal was useless. The liquor was not suitable for paper-sizing. Schacht said that Leowe, Berlin, was using only 5 tons of liquor yearly for briquetting sand moulds. Schott had not found the liquor good for binding cement. Ferenczi said that a Hungarian coke-oven factory had used the liquor for briquetting but had given it up. Steinbock held that the use of evaporated sulphite liquor as a fuel was not practicable on account of the large amount of ash and the bad odour. The amount of liquor used in Mitscherlich's factory according to Mitscherlich's patents amounts to 3 per cent of the output of that factory.

Papier-Ztg. vol. 30 (1905) p. 1961.

Griffin, M. L.—WASTE FROM PULP-MILLS AND PAPER-MILLS.

Extracts from paper read before International Congress of Applied Chemistry. General discussion of waste waters from soda mills and sulphite mills.

Pulp Paper Mag. Can. vol. 4 (1906) p. 75.

Konig, J.—POLLUTION OF WATERS AND UTILIZATION OF WASTE SULPHITE LIQUOR.

Z. angew. Chem. vol. 19 (1906) p. 750.

Leisenberg, C.—PURIFICATION OF WASTE SULPHITE LIQUOR WITH MILK OF LIME, FERRITE, AND ALUMINATE.

Schubert, Zellstoffabrikation (1906) p. 253.

Vogel, J. H.—WASTE LIQUORS AND WASTE WATER FROM SULPHITE MILLS.

((See " Effluents " p. 35.)

Little, A. D.—PROGRESS IN THE MANUFACTURE OF SULPHITE PULP IN 1906.

Experiments with waste liquor as a dust binder for roads, binder for moulding sand, tanning material.

Papier-Fabr. vol. 5 (1907) p. 649.

Schwalbe, C. G.—LITERATURE AUSZUGE.

An abstract of literature connected with the pulp and paper industry and published annually by the German Association of Pulp and Paper Chemists. Volume I, 1909, also contains literature on the waste sulphite liquor.

Phelps, E. B.—THE POLLUTION OF STREAMS BY SULPHITE PULP WASTE. (A STUDY OF POSSIBLE REMEDIES).

The author discussed the question of stream pollution by sulphite pulp liquor referring more particularly to conditions in the United States. A summary of the literature, taken for the most part from Cross and Bevan, Researches on Cellulose, and Seidel's Papers is given. The author investigated the action of phosphorous pentachloride on the lignin sulphonate and did not observe any reaction. No results were obtained on investigating the fusion of the lignin sulphonate with alkalies. The author tried to purify the products resulting from the treatment of the liquor with a large number of aromatic amines. The Diazo reaction was applied to these condensation products but without result. The action of nitric acid on waste liquor was tried and it was found that a yellow solution was produced, due to what the author calls lignum-yellow, which was capable of dyeing wool and silk. This colouring substance was isolated by evaporating the solution in vacuo. It is a light yellow powder, very porous and extremely hygroscopic. When dried at 100° it is decomposed with evolution of nitrous oxide. It can eventually be oxidized with nitric acid to oxalic acid. Attempts to reduce this substance by various means resulted in failure. This substance was also treated with amines, resulting in the production of various coloured substances. An attempt was made to prepare sulphur dyes from sulphite liquor by heating lignin sulphonate, sodium sulphide, and sulphur. A green powder resulted which seemed to act as a true sulphur dye. In place of the lignin sulphonate, some of the above mentioned amine condensation products were used, but with no different result.

Water Supply Paper 226, Government Printing Office, Washington.
The Paper-mill vol. 32 No. 2 p. 19.
Papier-Ztg. vol. 34 (1909) p. 726.

Pritzkow, A.—THE PRESENT SITUATION OF THE WASTE WATER PROBLEM IN THE SULPHITE MILLS.

In the production of 100 kilogrammes (220 lb.) of cellulose 1,000 litres (220 gallons) of sulphite liquor are produced. Some other general figures given. Mentions different proposals for utilization of liquors.

(See " Effluents " p. 35.)

Stutzer, A.—WASTE SULPHITE LIQUOR.

Z. angew. Chem. vol. 22 (1909) p. 1999.
Chem. Abs. vol. 4 (1910) p. 107.

Klein, A.—DISCUSSION ON WASTE SULPHITE LIQUOR AT THE ANNUAL MEETING OF THE GERMAN PULP AND PAPER CHEMISTS 1909.

Papier-Ztg. vol. 34 part I (1909) p. 227.
Wochbl. Papierfabr. vol. 40 (1909) p. 240.

Kumpfmiller, A.—WASTE SULPHITE LIQUOR.

Contains a description of evaporation apparatus for sulphite liquor.

Thesis, Munchen 1909.

WASTE LIQUOR PROBLEMS.
Papier-Ztg. vol. 35 (1910) p. 2075.

EFFLUENTS FROM PULP-MILLS.
World's Paper Trade Review (1909) No. 3, p. 36.

Fischer, E. J.—THE WASTE LIQUOR FROM SULPHITE MILLS.
A technological study.
Papier-Kalender Pfaff-Lohne, 1910.

Frank, A.—SOLUBILITY OF CALCIUM MONOSULPHITE IN WATER.
Papier-Ztg. vol. 35 (1910) part I p. 145.

Stutzer, A.—INVESTIGATIONS ON WASTE SULPHITE LIQUOR.

a. Determination of sulphurous acid. Acetic acid recommended instead of phosphoric acid for driving off the SO_2. Description of method of analyses.

b. Removal of the sulphurous acid from the waste liquor. In order to reduce the amount of ash substances ammonia is recommended. By evaporation to dryness all sulphurous acid that can be driven off with acetic acid is removed.

c. By addition of calcium carbonate only part of the ammonia is recovered. A large quantity remains in the residue.

d. Considerably more calcium sulphite can be precipitated with ammonia than with lime sludge.

Papier-Ztg. vol. 35 (1910) part II pp. 3091, 3167.

Sander, A.—PROGRESS IN THE CHEMISTRY AND INDUSTRY OF CELLULOSE 1909-1910.
A review of literature on utilization of waste sulphite liquor.
Fortschritte Chemie, vol. 4 (Gebr. Bornträger Berlin 1911) p. 300.

WASTE SULPHITE LIQUORS.

General Discussion of the utilization of waste sulphite liquors, with notes on the following methods of utilization:

(1) wood preservatives, (2) tanning materials, (3) road binder and briquettes, (4) sizing paper, (5) alcohol. Canada could produce 1,800,000 gallons of industrial alcohol worth $1,000,000 and the United States could produce 11,000,000 gallons worth $6,000,000.

Pulp Paper Mag. Can. vol. 10 (1912) p. 45.

WASTE SULPHITE LIQUORS.

A criticism of the article on "Waste Sulphite Liquors" in the Pulp and Paper Magazine of Canada, vol. 10 (1912) p. 45. The writer states that the use of the liquor for alcohol does not solve the problem, as the waste discharged into small rivers from the alcohol plants is much more disastrous than the original waste. He regards its use as tanning and wood-preserving material as the more useful in eliminating discharge troubles. He claims that when wood is treated with waste liquor as part of the preserving material, and dried, it takes a much better finish, is harder in character, and is more highly lignified.

Pulp Paper Mag. Can. vol. 10 (1912) p. 176.

DEVELOPMENT OF CHEMICAL WOOD-PULP INDUSTRY IN SWEDEN AND RECLAIMING OF BY-PRODUCTS.

Article contains general notes on the various attempts to utilize waste sulphite liquor.

Pulp Paper Mag. Can. vol. 10 (1912) p. 314.

Muller, M.—LITERATURE ON WASTE SULPHITE LIQUOR.

"Literatur der Sulfitablauge" Berlin 1911 giving patents and literature on Waste Liquor up to 1911.

Hutchins, E.—METHODS OF TREATING PAPER-MILL WASTES.

Refers to waste sulphite liquor. Very complete articles on paper-mill waste as treated in United States.

Paper vol. 13 (1913) No. 3 p. 17; No. 4 p. 15; No. 5 p. 17.
Chem. Abs. vol. 7 (1913) p. 2855.

Muller, M.—RECENT RESEARCHES ON THE WASTE SULPHITE LIQUOR PROBLEM.

Wochbl. Papierfabr. vol. 44 (1913) p. 2206.
Chem. Abs. vol. 7 (1913) p. 3022.

Walker, W. O.—THE PROBLEM OF THE WASTE LIQUORS FROM SULPHITE PULP-MILLS.

General discussion of processes of utilization.

Suggestion for research.—In spite of the fact that a tremendous amount of work has been done on the subject, the problem still remains for the most part unsolved. It is to be noted that most of the investigative work that has been carried on in the past has not been for the purpose of determining the actual structural relations existing in the molecule of the main constituent of the organic substance of the waste liquor. This accounts, no doubt, for the meagre knowledge we possess of this substance. We can scarcely hope to make much advancement in the utilization of this substance until we know more about its composition. What we need is more purely scientific investigation into the structure of the main organic substance. It is true that such an investigation is beset with great difficulties, owing to the inertness of the substance towards solvents. Attempts should be made toward recovery of the sulphur on the understanding that it is in the form of a sulphonic group.

At present this seems to be a chemical impossibility. If such could be accomplished, however, the cost of the production of pulp would be considerably reduced. The work of the amine condensation products should be extended with the purpose of solving their structure, as well as for working up useful substances from them.

Further work might be done to try to increase the amount of fermentable material for the production of alcohol. The subject of its use in the treatment of roads should be investigated more fully and on existing roads. Its possible use as a binding material should be tried with a larger number of materials. In connection with this, a method for making it waterproof would be a great help. A patent has lately been granted for obtaining hydrocarbons of formula C_5H_8, and multiples thereof, from carbohydrates. As the liquor contains carbohydrates it would be possible to obtain turpentine and, consequently, rubber from the liquor. This should be investigated more fully. In fact, it might well form the subject of a research to be undertaken by the Canadian Government in connection with the conservation of our natural resources.

J. Soc. Chem. Ind. vol. 32 (1913) p. 389.
Chem. Eng. vol. 17 (1913) p. 246.
(See "Tanning Materials" p. 78, "Binding Materials" p. 52, and "Dye" p. 148.)
Paper vol. 11 (1913) No. 9 p. 21.

Klein, A.—PROGRESS IN CHEMICAL PULP INDUSTRY.

Deals with various improvements in the cooking process and in the digesters, and also discusses the waste liquor. Of the numerous proposals for the utilization of waste liquors for the manufacture of tanning materials, fertilizers, feeding stuffs, dyes, alcohol, etc. the author states that none has given practical results; the most promising are the processes devised for alcohol production (see J. Soc. Chem. Ind. vol. 29 (1910) pp. 810, 1052, 1265). Strehlenert's process (J. Soc. Chem. Ind. vol. 12 (1913) p. 652) seems to be practicable. In this the sulphite liquor yields alcohol, plaster of Paris, sulphur dioxide and a fuel with a calorific value of 7,000 calories (12,600 B.T.U.). By Rinman's process (see J. Soc. Chem. Ind. vol. 31 (1914) p. 307) 500 kilogrammes (1,100 lb.) of "carbon", 100 kilogrammes (220 lb.) of spirit and acetone, and 100 kilogrammes (220 lb.) of motor spirit are said to be recovered per metric ton (2,204 lb.) of cellulose.

Papier-Fabr. vol. 12 (1914) pp. 601, 639.
J. Soc. Chem. Ind. vol. 33 (1914) p. 1201.
Paper vol. 14 (1914) No. 22 p. 15; No. 23 p. 16; No. 24 p. 22; No. 25 p. 17.

Lassar-Cohn.—THE PROBLEM OF UTILIZATION OF WASTE WATER FROM THE SULPHITE MILLS.

The addition of waste liquor to the city sewer for irrigation fields has proved successful in Konigsberg (Germany). Leading the waste liquor into the Haff has proved beneficial to the fish.

Chem.-Ztg. vol. 38 (1914) pp. 639, 657.
Paper vol. 14 (1914) No. 17 p. 23.

Gottstein, L.—THE PROBLEM OF UTILIZATION OF WASTE WATER FROM SULPHITE MILLS.

A criticism of the Lassar-Cohn article.
Chem.-Ztg. vol. 38 (1914) p. 804.

Scott, J.—UTILIZATION OF WASTE SULPHITE LYE.

Paper-Maker British Trade J. vol. 47 (1914) p. 395.
Chem. Abs. vol. 8. (1914) p. 2620.

Muller, M.—LITERATUR DER SULFITABLAUGE.

A collection of literature upon the waste sulphite liquors problem from 1910 to 1913.

Güntter-Staib, Biberach, 1914.

Bryant, O. F.—SULPHITE PULP LOSSES.

Paper read before Canadian Pulp and Paper Association. Short description of Kumpfmiller's process for tanning, Ekstrom's alcohol process, and Strehlenert's fuel process.

Pulp Paper Mag. Can. vol. 13 (1915) p. 139.
Paper, vol. 15 (1915) No. 26, p. 15.

McKee, R. H.—PROGRESS IN PAPER-MAKING CHEMISTRY.

Note on sulphite waste liquors. Two mills in the United States are producing alcohol from the waste liquor. The yield is about 15 gallons (U.S.) of 95 per cent alcohol per ton of sulphite pulp. The slops are as objectional as the original waste liquor.

Pulp Paper Mag. Can. vol. 13 (1915) p. 165.

Dickerson, W. H.—THE DISPOSAL OF WASTE SULPHITE LIQUORS.

Paper read before the Technical Association of the Pulp and Paper Industry. Discussion of the problem in a general way: Robeson Process Co., International Paper Company (binder); West Virginia Pulp and Paper Co., N.Y. (alcohol); Crown-Willamette Paper Company and Kimberley-Clark Co. (development work on alcohol).

"Whatever use or uses are to solve the problem, it is not going to be the dye industry or similar outlets consuming a small quantity of high-class materials. It will rather be by some use or uses that will consume a large tonnage at a very small margin of profit."

The sulphite production in the United States amounts to about 4,500 tons per day which involves the production of approximately 7,500,000 imperial gallons of waste sulphite liquor containing 4,500 tons of solid material. It was shown in the discussion that for each ton of pulp about 1,500 pounds of solid matter drained off and this could be increased to 2,000-2,100 pounds by the use of special apparatus.

Paper vol. 19 (1917) No. 20 p. 19, No. 21 p. 17.

Bates, J. S.—PRESENT AND POSSIBLE PRODUCTS FROM CANADIAN WOODS.

Possible products of waste sulphite liquors. With Chart.

Pulp Paper Mag. Can. vol. 15 (1917) p. 553.

INDEX OF AUTHORS

PUBLICATIONS ISSUED BY THE FORESTRY BRANCH

Annual Report of the Director of Forestry, 1914-15-16-17.
Bulletin 1. Tree-Planting on the Prairies.
" 8. Forest Products of Canada, 1908.
" 11. Forest Products of Canada, 1909: Lumber, Square Timber, Lath and Shingles.
" 12. Forest Products of Canada, 1909: Pulpwood.
" 14. Forest Products of Canada, 1909: Cross-ties Purchased.
" 15. Forest Products of Canada, 1909.
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" 33. Forest Conditions in the Rocky Mountains Forest Reserve.
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" 56. Forest Products of Canada, 1914: Lumber, Lath and Shingles.
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