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Yeast from citrus waste syrup for stock feed : ?b ethyl cellulose lacquers for plastic coating and ethyl cellulose automotive lacquers.

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UNIVERSITY OF LOUISVILLE

YEAST FROM CITRUS WASTE SYRUP FOR STOCK FEED
ETHYL CELLULOSE LACQUERS FOR PLASTIC COATING
AND
ETHYL CELLULOSE AUTOMOTIVE LACQUERS

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of the Graduate School
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Department of Chemical Engineering

By
Walter Zabban
1944

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ABSTRACT

This report is on three projects: the Production of Yeast from Citrus Waste Syrup for Stock Feed, the Development of Ethyl Cellulose Lacquers for Molded Plastics, and Automotive Lacquers using Ethyl Cellulose.

The purpose of the first project was to find a method of utilizing citrus syrup for the production of yeast for fortified feed. The syrup is the only product in processing of citrus wastes for cattle feed. A "Torula Utilis" strain of yeasts was used, and optimum conditions were determined for its growth.

The second project was the development of a white Ethyl Cellulose lacquer for protective coating of objects made of Ethyl Cellulose molded plastics.

The third project was a continuation of previous work conducted in the laboratory on formulating a cheap Ethyl Cellulose lacquer for the Automobile Industry. The original formulae (4) for a gray sanding surfacer and a black top coat were modified, using cheaper resins and cheaper solvents. Colored lacquers were also investigated.

YEAST FROM CITRUS WASTE SYRUP FOR STOCK FEED

INTRODUCTION

Citrus Waste consists of the peel, rag, and seeds resulting from sectioning and juicing of citrus fruits.

The disposal of citrus waste is an important matter in California and Florida where citrus fruits are abundant. In many localities the plants are not located near satisfactory sewage disposal units and the maintenance of sanitary conditions requires the satisfactory disposal of waste. Its disposal is not similar to that of ordinary sewage because of its high biochemical oxygen demand.

Various chemical processes have been investigated in the past five years with the purpose of manufacturing a useful by-product from citrus waste. A complete study of the utilization of citrus waste has been prepared and is shown in Appendix I. The production of stock-feed yeast has been investigated because it is of particular interest in our wartime economy. Previous investigations had been carried out on blackstrap molasses (19) for production of yeasts for food purposes. The results obtained suggested that citrus waste could also be used for the same purpose. "Torula Utilis" yeast was selected because of its low alcohol yield. A study was undertaken for the purpose of establishing the best conditions of sugar concentration, aeration, temperatures, and hydrogen potentials.

HISTORICAL

The production of yeasts constitutes one of the most ancient industries of the world. Baking, brewing and wine making have been practiced for many centuries by Egyptian, Jewish, Greek, and Roman people. It has constituted the first indirect use of yeast. Mason, an Englishman, is said to have prepared the first compressed yeast in 1792. No hops were used in its manufacture. Shortly thereafter, compressed yeast was known in Holland and in Germany as well as in England. Indeed, there is some evidence that compressed yeast was made in Holland as early as 1781. Some (11) consider the date of the first compressed yeast industry as being 1870. In this year was developed the Vienna process in which, kiln dried malt and corn were ground, mixed with water, and mashed. The unfiltered mash was pitched and permitted to ferment. Machines separated the portions of grain from the yeast by a process of sifting. Yields of 10 to 14% on the basis of the grain were obtained with a yield of about 30% alcohol. Today yeasts are produced by the molasses-ammonia process where the amount of alcohol produced is limited. The molasses mash is carefully prepared. If the molasses is deficient in phosphorus, ammonium or calcium phosphate is added. Phosphorus is important in the synthesis of nucleo-proteins by the yeast and in buffering the medium;

it also stimulates growth. Throughout the run, the pH and the temperature of the wort are carefully controlled (19). At the end of the growing process, yeast is separated from the wort by the use of centrifugals. The yeast thus obtained is washed repeatedly, until the wash water is quite clear. It is then pressed.

Yeast can also be prepared from sulphite liquor (5) and from wood sugar (22).

The citrus process is analogous to and competitive with the molasses-ammonia process. The citrus syrup method has been developed in the last two years, and it is being studied with the idea of commercial production. The citrus syrup is the concentrate of the juice obtained from the liming of waste.

During the 1940-1941 season, 35,000 tons of dry feed were produced in Florida (15). The discarded juice obtained in producing this feed represents a waste of nearly 35,700,000 lbs. of sugar (sucrose and reducing sugars), 2,490,000 lbs. of protein and nearly 3,800,000 lbs. of pectin. The quantity of press juice obtained per ton of dry feed is approximately 1,800 gal.

It is possible by fermenting such juice to decrease its five days biochemical oxygen demand from 40,000 to 65,000 ppm. to 2,500 and 10,000 ppm. Citrus syrup has a sugar concentration of 36% the result of an evaporation of citrus press juice from the liming process (10) of citrus waste.

The production of feed yeast has been investigated. Several strains of yeasts were experimented, viz., "Saccharomyces Ellipsoideus", "Saccharomyces Sake", and "Torula Utilis". This last has been selected because it propagates rapidly with $(NH_4)_2SO_4$ as a nutrient, and because it produces very little alcohol. Its use as an industrial organism is not new, since it was grown on a commercial scale in Germany during the war period 1914 to 1918 as a feed material (7).

THEORETICAL

"Torula Utilis" is called a false yeast because it is incapable of producing spores. Its value lies in the fact that it produces high protein food, useful when animal protein is not available. The protein of this yeast is said to be biologically complete protein. An analysis of the dry matter indicates that protein constitutes slightly more than 50% of the dry weight. The proteolytic digest of yeast yields a product that is meat-like and contains vitamin G in large quantities.

"Torula Utilis" has the ability to assimilate pentoses (11), to synthesize vitamin B complex (21), nicotinic acid, and gluthatione (6) from sugar and mineral salts in the nutritive medium. Its content of vitamin B complex is higher than that of animal protein, including liver. The indications are that the yeast will abstract vitamin B_1 from the medium, when it is thus available, in preference to synthesizing it. The vitamin B_1 potency is increased when aeration is not used during the fermentation process, but the yield of yeast is small under such conditions.

"Torula Utilis", like all yeasts, contains fat in which are found the following constituents: palmitic oleic, linoleic, and lauric acids; the phospholipids, lecithin and cephalin; ergosterol, zymosterol, and other components. Nucleic acid, phosphates, and potassium salts are present in small quantities. The first is used for medicinal purpose, the other two are used as valuable food components.

EXPERIMENTAL

Equipment:

The yeast was incubated in glass bottles; an air compressor supplied air for aeration; the air flow was measured with a gas meter; a De Laval Oil Centrifuge Model AE was used for the concentration of yeast; a standard hemocitometer and a binocular Bausch and Lomb microscope was used for yeast cell counts; the pH was determined with a Beckmann pH meter; mechanical agitation was furnished by a Turbo-Mixer. Later, fermentation was carried out on a small pilot plant scale and sterilized 20 gal. crocks were used for yeast incubation.

Procedure and Results:

The first work was the preparation of a malt starter: 300 g. of finely ground malt hops were mixed into 2000 cc. of distilled water. The mixture was gently heated to 145°F and kept at that temperature for 10 min., to effect a maximum malt conversion. It was then heated to boiling. The malt mixture was filtered hot through cheese cloth and refiltered through a burlap cloth. The malt filtrate was sterilized and cooled. When the temperature was about 78-85°F, 25 cc. of filtrate were poured into a sterilized test tube and inoculated with a loopful of "Torula Utilis" yeast strain from a Difco Agar slant. The test tube was immediately plugged with sterilized cotton. It was slowly rotated around its vertical axis to insure better and faster propagation. After two hours, the inoculated solution was carefully poured into a 500 cc. Erlenmeyer flask containing 300 cc. of malt mixture; care was taken to avoid any possible contamination. Air was introduced into the Erlenmeyer flask at a rate such as to provide uniform agitation and good oxygen absorption. The air was filtered through glass wool and water.

The incubation of the starter lasted 4 hours and the malt mash was poured into a 2½ l. bottle, half of which had been previously filled with malt mixture. Filtered air was introduced at the rate of 0.25 cu. ft. per gal. per min. The final incubation lasted 24 hours. The yeast starter was later placed in a refrigerator and kept at 7-9°C for a week; this was done to obtain a high yield of bottom yeasts.

Citrus waste syrup - 72% solids, 50% total sugars - was diluted to the desired sugar concentration with tap water and heated to boiling. It was filtered through cheese cloth and sterilized; it was cooled to room temperature and inoculated with 4% by vol. of malt starter. Nutrients were added, 9% by wt. of Na_3PO_4 (based on the weight of total sugars), and 16% by weight of $(NH_4)_2SO_4$. Only 50% of the ammonium sulfate was added at the start, to avoid unnecessary foaming, the rest was added during the fermentation in a period of 4 hours. The batch was air agitated. The air rate was kept constant within 0.05-0.08 cu. ft. per gal. per min. because the purpose was to observe the rate of yeast growth as a function of time, keeping all the variables constant. The sugar concentration was 1%; a yeast count was taken every hour, for the purpose of determining the economical and optimum length of fermentation. A yeast count is the number of yeast cells present in 1 cc. of liquid. The results obtained are shown in Table I.

Additional experiments were conducted with the same initial conditions. These runs showed that after 24 hours fermentation, the yeast growth remained constant; its growth was not only hindered but actually the surrounding medium became toxic, causing suffocation of the living cells. A summary of the results obtained is shown on Table II.

A five day biochemical oxygen demand was determined for the fermented and unfermented press juice which is diluted syrup. The results were respectively 220,000 ppm. and 280,000 ppm., based on the concentrated syrup.

The fermented solution was centrifuged to concentrate the yeast to 50% moisture. The yeast was slowly dried in a vacuum oven at 60°C; its percentage based on the weight of total sugars was determined and found to be 41.82.

TABLE I

INCREASE IN YEAST COUNT WITH TIME OF FERMENTATION

Time (hrs.)	Temperature (°C)	Yeast Count ($x10^{-6}$)	pH
0	23.0	4	6.55
1	25.0	8	6.50
2	24.5	13	6.40
3	26.0	16	6.30
4	25.5	20	6.15
5	25.0	26	6.05
6	25.0	26	5.85
9	23.0	42	5.28

TABLE II

RATE OF YEAST GROWTH DURING FERMENTATION

Time (hrs.)	Temperature (°C)	Yeast Count ($x10^{-6}$)	pH
0	24.5	4	6.5
2	24.0	14	6.3
4	24.0	19	6.0
6	24.0	25	5.5
24	23.0	127	4.5
28	23.0	125	4.5
32	20.0	126	4.7

TABLE III

YEAST GROWTH WITH VARIATION IN SUGAR CONCENTRATION*

% Sugar	Yeast Count after 5 hrs. $(x10^{-6})$	Yeast Count after 9 hrs. $(x10^{-6})$	Yeast Count after 24 hrs. $(x10^{-6})$
1	27	55	55
2	32	65	88
3	37	87	180
4	21	52	101
5	21	50	-
6	18	40	75

TABLE IV

YEAST GROWTH WITH VARIATION IN RATE OF AIR FLOW

% Sugar	Air Rate of Flow (cu.ft./gal./min.)	Yeast Count after 20 hrs. $(x10^{-6})$	pH
3	0.157	80	5.8
3	0.390	104	4.1
3	0.832	314	4.1
3	1.022	180	5.8

* Air rate was kept constant at 0.55 cu. ft./ gal.

In the previous experiments, aeration and sugar concentrations had been kept constant. It was decided to study the effect of variation in sugar concentration on the yield of yeasts when the rate of air flow was kept constant. The results obtained (Table III) showed that when the concentration of sugar was 3%, the highest yield of yeast was obtained. For the same rate of air flow 2% and 4% sugar concentrations gave lower counts. This concentration was therefore kept constant in the following runs while the rate of air flow was varied. The results obtained are shown in Table IV.

An experiment was later conducted on a small pilot plant scale. Three 20 gallon crocks were sterilized and half filled with 10 gal. of citrus waste syrup, containing 3% sugar. This run was made with the purpose of determining whether a mechanical agitation was more efficient than air agitation. It was found that the yields obtained with mechanical agitation were slightly higher than those given by air agitation, but that such results did not justify the use of surplus equipment.

CONCLUSIONS

The use of citrus waste syrup is recommended for the production of yeast for stock feed. It is evident from the results obtained that a dilution of the syrup to a sugar concentration of 3% will give the best fermenting conditions if some variables are carefully controlled; the amount of dry yeast obtained by such fermentation is approximately 42%, based on the weight of the total sugar.

The variables to be controlled are aeration, temperature, pH, and agitation. The air should be sterilized and introduced in the fermenting tank at the rate of 0.8 cu.ft./gal./min.; the rate of flow can be varied depending on the size of the tank, but the variation should not be greater than 0.2 cu. ft./gal./min. because a minimum amount of oxygen should be introduced per pound of dry yeast produced. The temperature should be kept between 88-90°F and the pH between 4-4.5; a lowering of the pH can be effected by the addition of sulfuric acid. Agitation should not be violent but rather uniform. The introduction of air is a method of producing agitation; mechanical devices can also be used, i.e., propellers and turbo-mixers. Mechanical agitation perhaps gives higher yields of product because it mixes more uniformly than air bubbling. Its disadvantage lies, however, in the overheating produced because of friction between the rotating paddles and the liquid. This factor contributes to a temperature rise of 20°F., and cooling coils must be used to keep the temperature of the fermenting tank within the optimum range.

A proposed plan for the production of yeast from citrus syrup on a commercial scale is shown in a flow sheet in the following page.

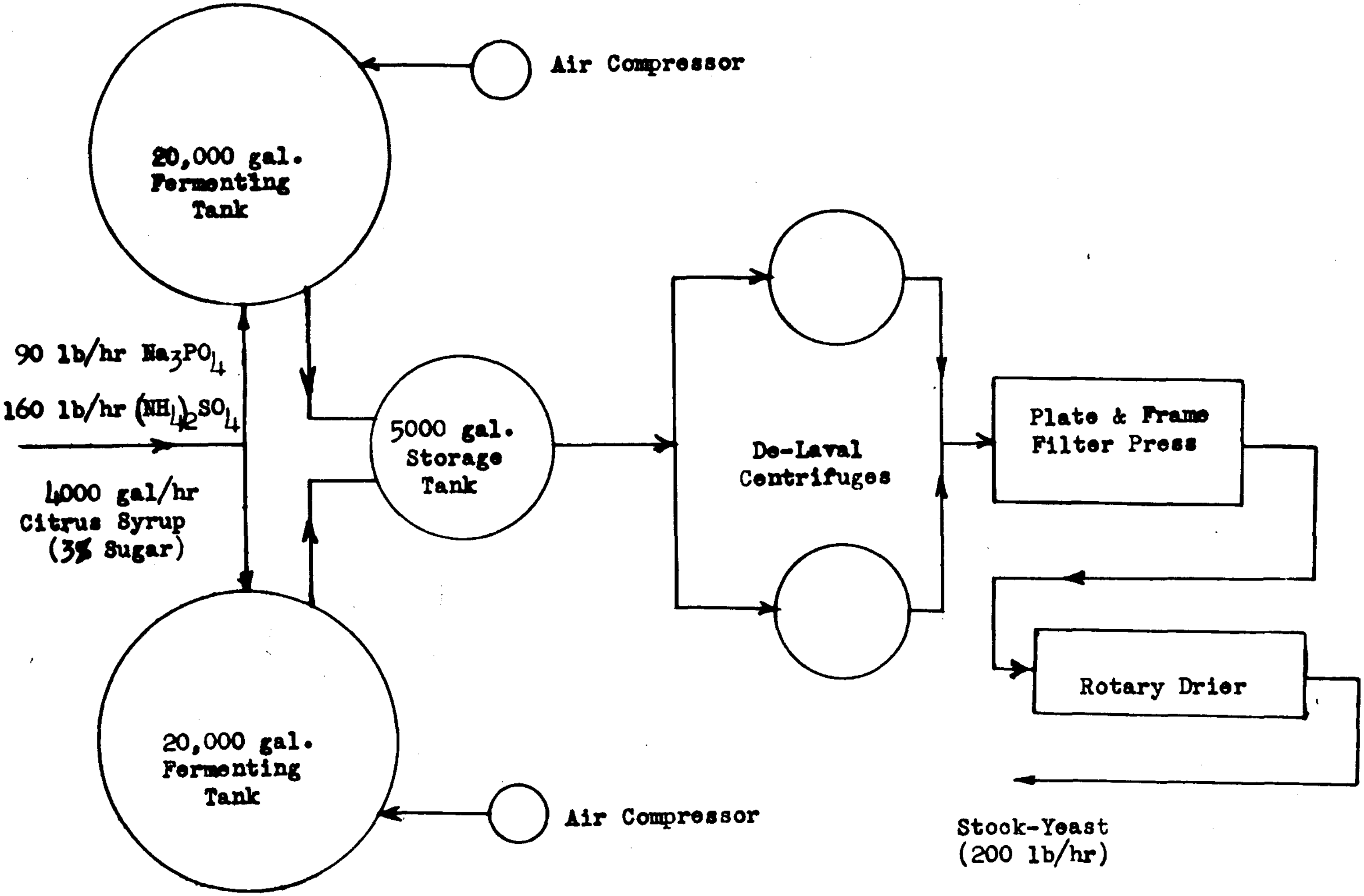

Fig. 1. Flow Sheet of the Production of Yeast from Citrus Waste

APPENDIX

Survey on Citrus Waste Utilization

This study was carried out with the purpose of suggesting research projects on the utilization of citrus waste.

The citrus industry is concerned with the industrial utilization of three citrus fruits: Lemons, Oranges, and Grapefruit. Two other fruits available in smaller quantities are citron and lime.

An approximate chemical analysis of the three main citrus fruits is shown in Table V. It is evident from such table that grapefruit has a composition which varies between that of orange and that of lemon.

It has been estimated that 8-10% of these fruits are directly processed for by-products; 25-30% are processed in canneries, from which the usual refuse, rag, peel, and seeds are discarded and the remainder sold for food products. On a tonnage basis this available waste amounts to approximately 1,000,000 - 1,200,000 tons per year in the United States.

The main by-products of the modern citrus industry are:

1. Citric acid and calcium citrate.
2. Fermentation products.
3. Pectin.

4. Essential oils.
5. Stock yeasts.
6. Vitamins.
7. Dehydrated waste for cattlefeed.
8. Marmalades and beverages.
9. Fertilizers.

In a series of accompanying flow sheets is shown a study of by-products that have been produced and possible new products. In Fig. 2 is shown the yield of possible products now known from each ton of waste.

A rough estimate of the price obtainable for the products of this citrus industry are given below. One ton of citrus waste could produce by-products which would sell for approximately $80.00 as compared to $3.50 obtained for a ton of waste converted into cattlefeed. The prices computed on the following materials are based on Fig. 2.

Pectin ($0.85 lb.); Ascorbic Acid ($11.00 lb.); Limonene ($0.48 lb.); Crude Grapefruit Oil ($2.00 lb.); Crude Lemon Oil ($3.25 lb.); Crude Orange Oil ($1.00 lb.); Terpeneless Lemon Oil ($25.00 - $50.00 lb.); Terpeneless Orange Oil ($97.00 - $100.00 lb.); Linalool ($6.75 - $7.00 lb.); Geraniol ($3.50 - $4.50 lb.).

TABLE V

ANALYSIS OF CITRUS FRUITS (26)

Content	Grapefruit %	Lemon %	Orange %
Water	88.8	89.3	87.2
Protein	0.5	0.9	0.9
Fat	0.2	0.6	0.2
Carbohydrates plus fiber	10.1	8.7	11.2
Sugar (invert)	6.5	2.2	8.8
Fiber	0.3	0.9	0.6
Ash	0.42	0.54	0.47
Acid (citric)	1.69	5.07	0.68

TABLE VI

GRAPEFRUIT WASTE ANALYSIS (2)

Material	Rag Per Cent	Peel Per Cent
Total solids	15.61	16.71
Ash	0.75	0.74
Acid as Citric Acid	0.63	0.74
Volatile Oils (Steam Distilled)	0.00	0.43
Ethyl Ether Ext.	0.16	0.28
Crude Fiber	1.44	1.71
Protein (Nx6.25)	1.06	1.13
Total Sugars (Invert)	6.30	6.35
Pentosans	0.44	0.83
Calcium Pectate	3.56	3.19
Naringin	0.10	0.40

Vitamins

Vitamins constitute quite a sizable industry today. There are means of producing these materials synthetically, but it is even more economical to extract vitamins from vitamin rich materials. Citrus fruits have always been a source of vitamin C. It has now been found that Vitamin C is not the only vitamin present in citrus fruits. Vitamins G and B are present in oranges and grapefruits; Vitamin A is present in oranges.

Vitamin C is of course present in larger quantities than the others. Grapefruit, for example, contains 20-30 mg. of Vitamin C per 100 g. of fresh peel. In lemon, Vitamin C is as high as 60 mg. per 100 g. of fresh peel.

Some research has been accomplished in the last year throughout the country on the extraction of Vitamin C by the use of an ion exchanger. Ion exchangers (14) have been used for years in large quantities for the softening of potable water and for production of organic salts from vegetable wastes, but the application of the ion exchanger theory to the commercial extraction of vitamin constitutes a new field of research.

Essential Oils

Essential oils are present in citrus fruits in percentages varying from 0.2 to 0.6%. An extraction of such oils would change the economy of citrus waste by-products.

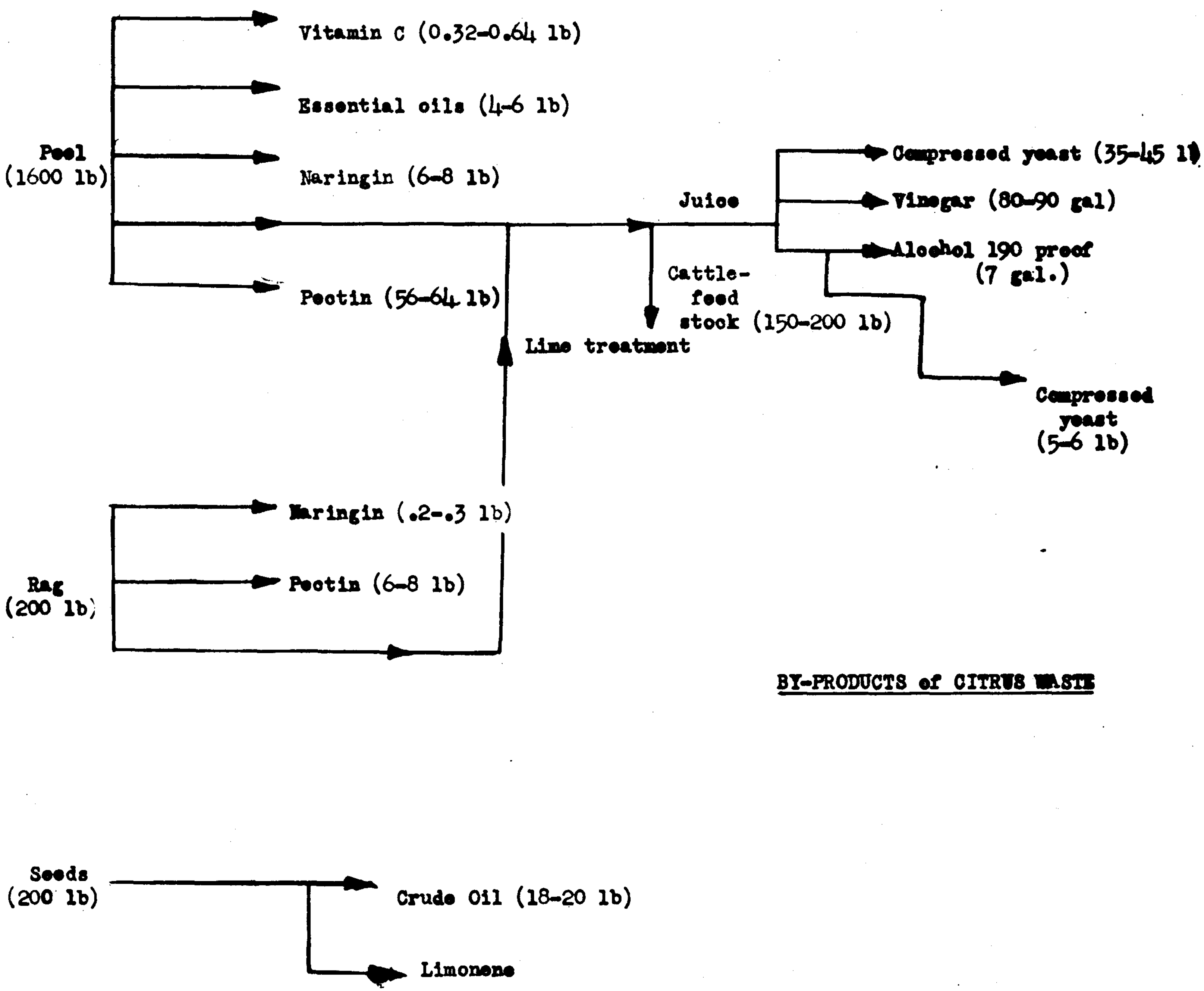

Fig. 2. By-Products of Citrus Waste

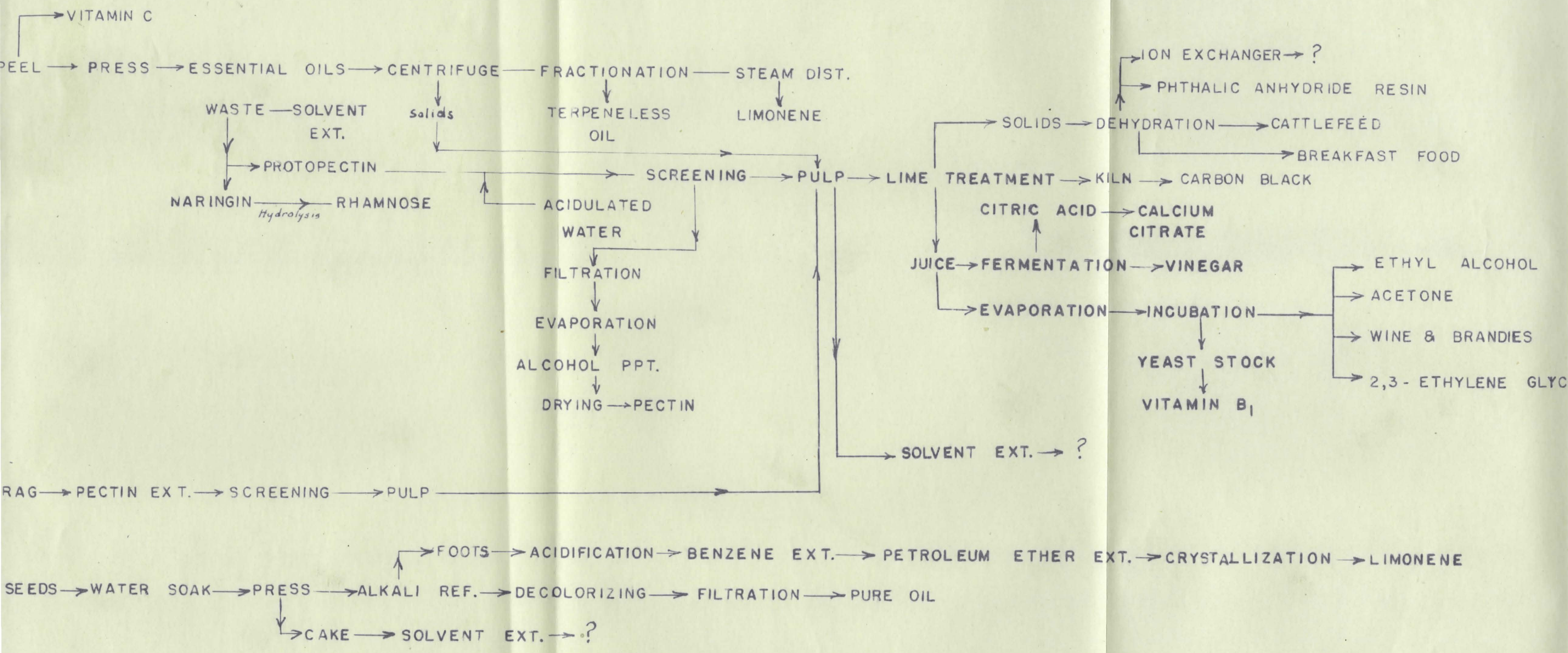
CITRUS WASTE DISPOSAL

Fig. 3. Flow Sheet of the Commercial Utilization of Citrus Waste

The chemical constituents of oil of lemon are: α-Pinene, β-Pinene, d-Limonene, γ-Terpenene, Citral; Acetic, Capric and Caprylic Acids; Bisabolene, Cadinene, Linalool, a Tertiary Alcohol $C_{10}H_{18}O$, an aldehyde, an amorphous compound (9,18).

The constituents of oil of orange are the following: Limonene; Decylic Aldehyde; Formic, Capric and Caprylic Acids; Octyl Alcohol, an Olefinic Alcohol $C_{10}H_{18}O$; Linalool; a white amorphous compound (9,18).

The chemical constituents of grapefruit oil are: Octyl and Decyl Aldehydes; Octyl Alcohol; Geraniol; Methyl Anthranilate; Citral and d-Cadinene (16).

The oil present in seeds is different from the volatile oil present in the peel. It consists of glycerides of palmitic, stearic, oleic, linolic, and lignoceric acids with some free acid and unsaponifiable matter. It has been found that it is possible by modern methods to produce one ton of crude oil per 10 tons of wet seeds (16).

Flow sheets for such an extraction process are shown in figures 4 and 5. A manual process like the one used in Sicily would extract approximately 80% of the total oil content of citrus fruits, while a mechanical process would yield 50% of the total oil content. A solvent extraction is not advisable in this particular case because of the relatively high cost incurred in the use of expensive solvents and also because of high oil coloration obtained.

RECOVERY of ESSENTIAL OILS from PEEL of GRAPEFRUIT

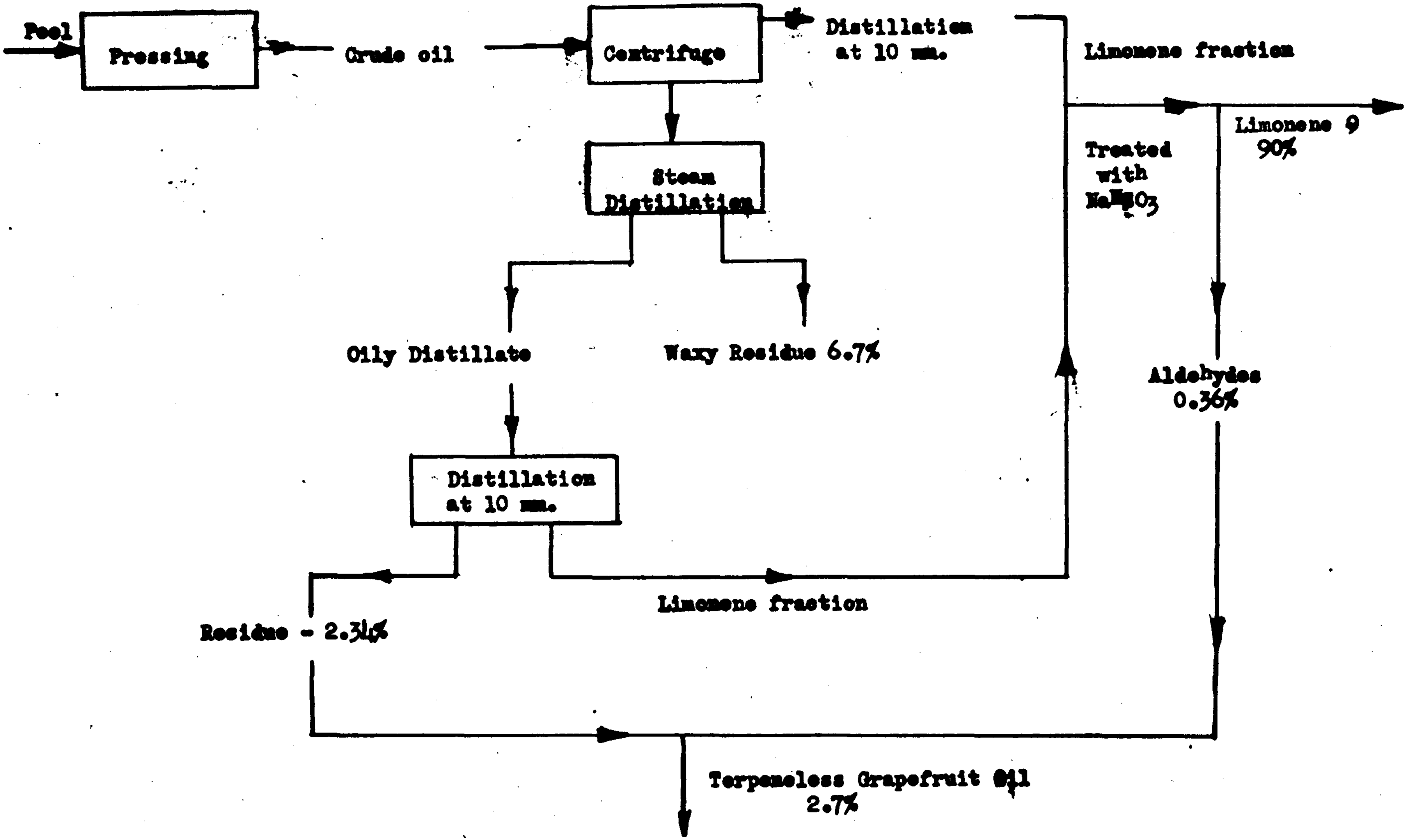

Fig. 4. Flow Sheet of the Recovery of Essential Oils From Peel of Grapefruit

EXTRACTION of OIL from CITRUS SEEDS

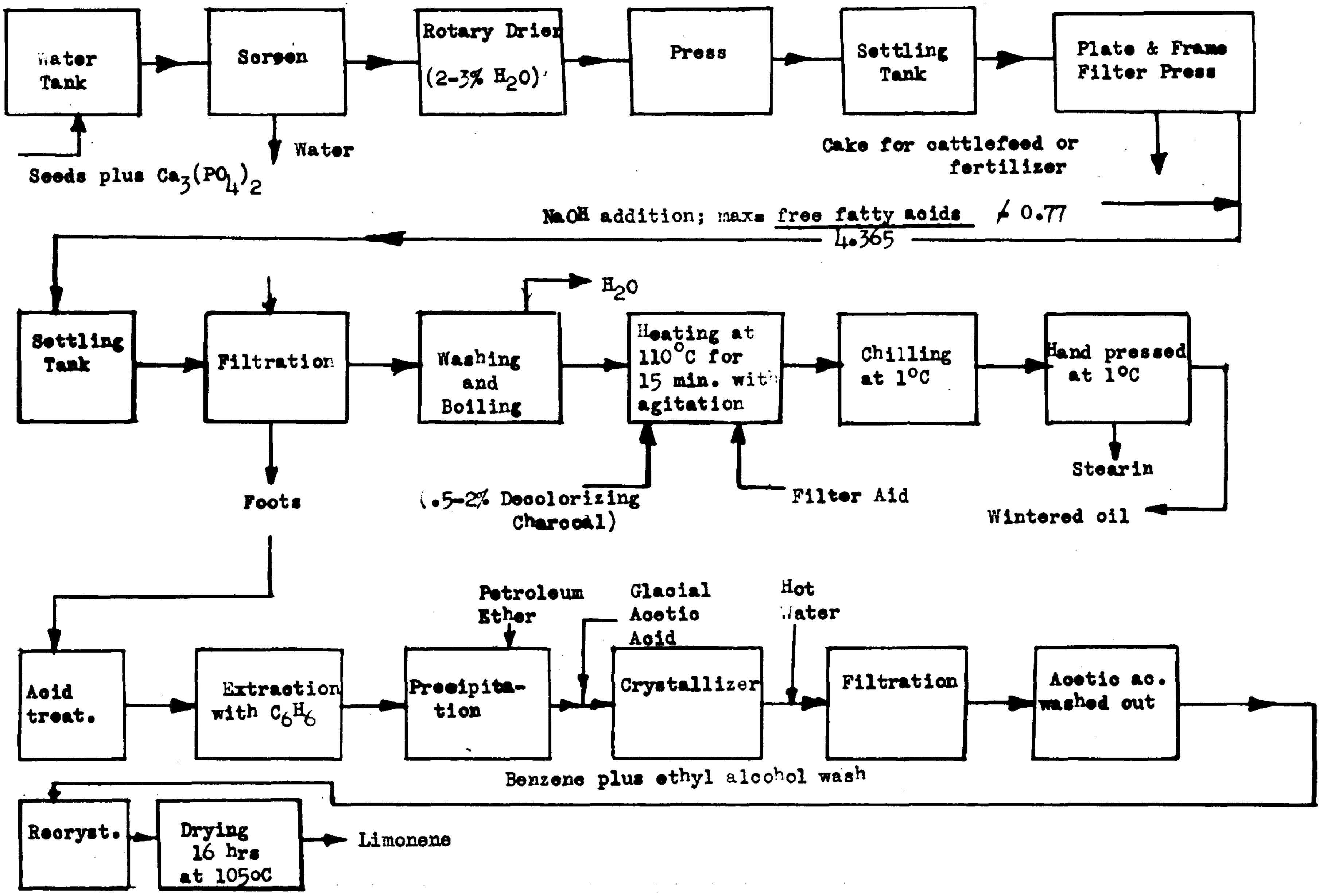

Fig. 5. Flow Sheet of the Extraction of Oil from Citrus Waste

Naringin

Naringin is found in relatively large quantities in grapefruit (Table VI) while hesperidin is found in lemons and oranges (25). The former is a bitter white crystalline glucoside which appears in the grapefruit blossoms, the latter is not so bitter, and its actual percentage in citrus fruits is unknown.

Naringin on hydrolysis yields naringenin and rhamnose. It is believed that phloroglucinol, which is found in small quantities in citrus fruits, is also a by-product. Phloroglucinol is used for medical purposes.

Flow sheets showing the extraction of naringin from citrus waste and its hydrolyzed by-product are in Figures 6 and 7.

Fermentation Products

The production of new materials by the fermentation of citrus waste with suitable microorganisms has encountered several difficulties in view of the low sugar content of citrus waste as compared with that of blackstrap molasses. It is true that citrus waste does not contain a comparable sugar percentage, but considering that a considerable amount of juice is wasted in the canning of citrus fruits and that

EXTRACTION of NARINGIN from CITRUS WASTE

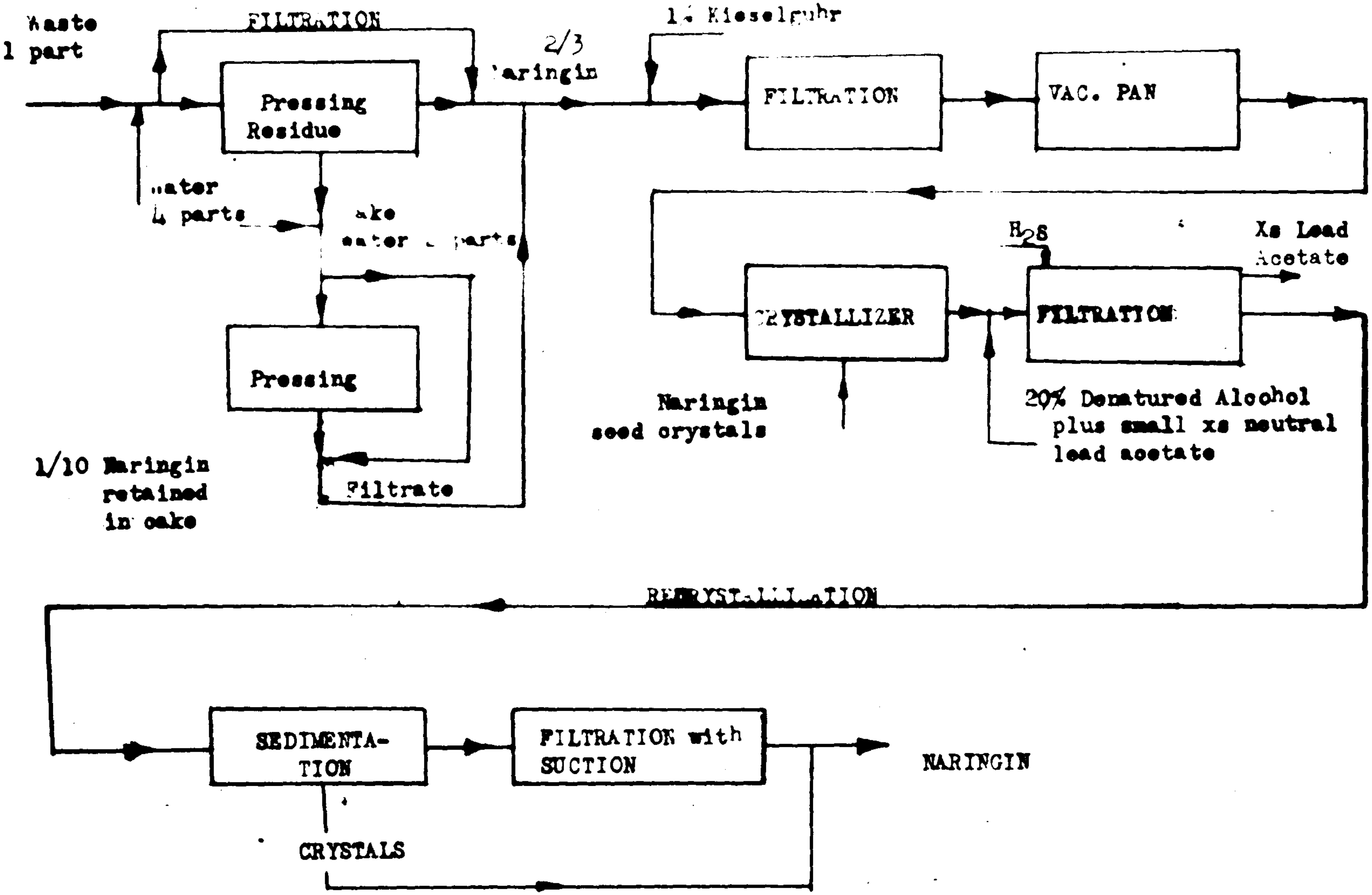

Fig. 6. Flow Sheet of the Extraction of Naringin from Citrus Waste

EXTRACTION OF RHAMNOSE FROM NARINGIN

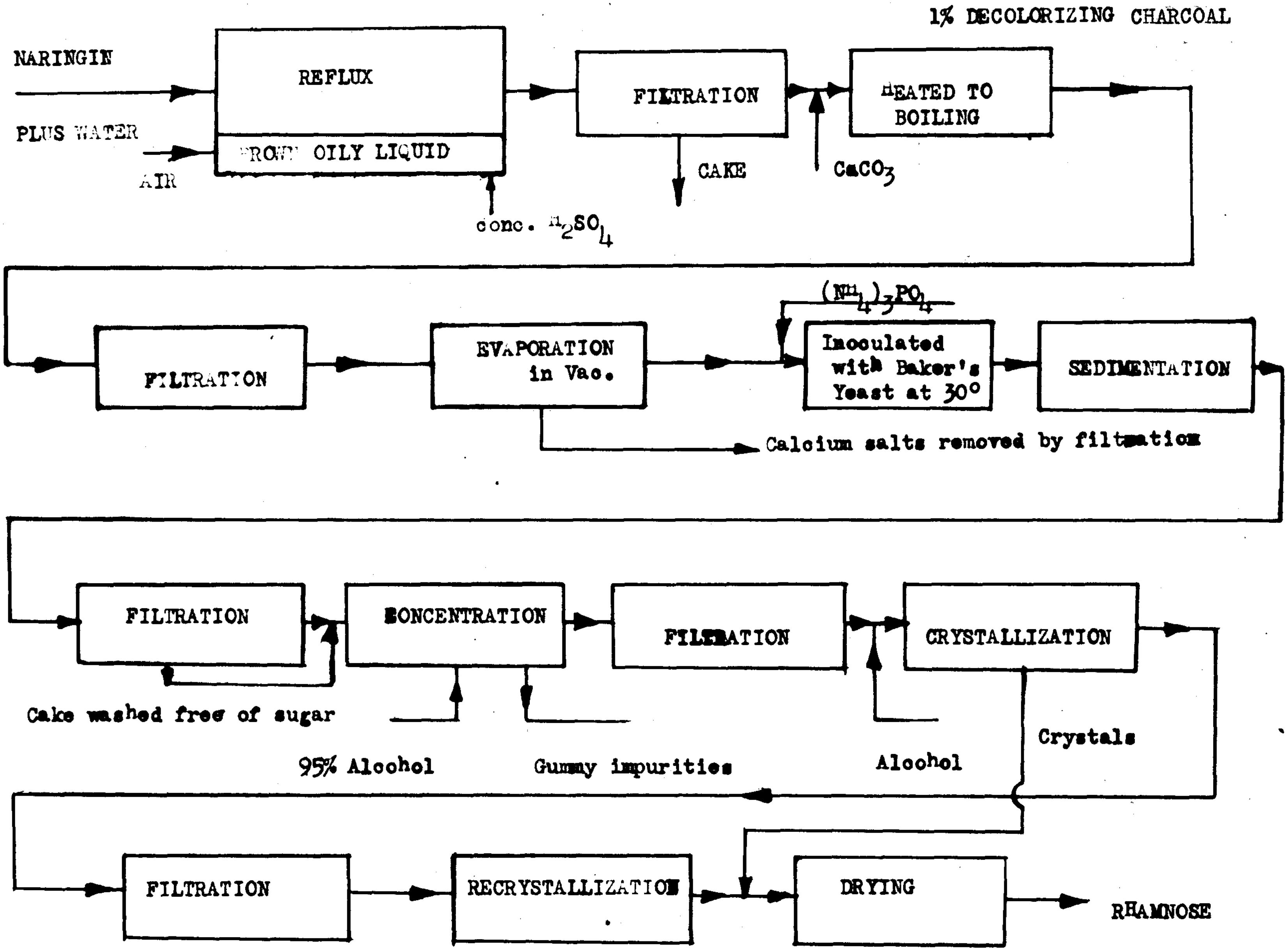

Fig. 7. Flow Sheet of the Extraction of Rhamnose from Naringin

the additional recovery of such juice would give a material with a sugar content as high as 80-85% of the soluble solids in the juice, it is entirely justified to stress the necessity of undertaking a thorough research on the study of fermentation. The sugars present in citrus fruits are glucose, mannose, dextrose, fructose, sucrose, raffinose, levulose, arabinose, xylose plus a few complex ones (25).

There is an article (15) in the literature in which it is reported that it is cheaper to manufacture 190 proof alcohol from citrus syrup than from molasses; such statement leads to arguments because it would seem that the contrary were true; nevertheless this shows that fermentation is feasible with citrus press juice. Good results are also reported in the production of acetone by fermenting the citrus syrup with "Clostridium Acetobutylicum" (20). Table VII shows the potentiality of press juice as a fermenting medium.

The production of yeasts as potential vitamin B_1 synthesizers is also performed by fermentation. In this particular instance, special strain of yeasts are chosen that do not produce a high amount of alcohol.

TABLE VII

APPROXIMATE COMPOSITION OF PRESS JUICE FROM CITRUS DEHYDRATION PLANTS IN FLORIDA (16)

Constituent	Max.	Min.	Av.
pH	6.4	5.4	5.7
Brix at 17.50°C	12.6	6.1	10.1
Total solids %	11.61	5.64	8.93
Volatile matter %	94.36	88.39	91.07
Sucrose %	3.09	1.20	2.40
Reducing sugars %	5.81	2.82	4.23
Total sugars %	8.58	4.08	6.63
Protein (Nx6.25) %	0.59	0.40	0.47
Pectin (Alcohol ppt.)	0.88	0.27	0.66
Pentosans %	0.42	0.23	0.31
Ash %	0.94	0.43	0.72
Fixed acid (citric) %	0.30	0.15	0.21
Volatile acid (acetic) %	0.78	0.01	0.14
Alcohol, % by vol.	0.39	0.00	0.22
Essential oil, % by vol.	0.58	0.12	0.23

Vinegar

Vinegar is now produced on a commercial scale. It does not compare with apple vinegar, but it is, nevertheless, sold in large quantities. The difficulty which arises in the citrus process is that the sugar content and the acetic acid content are not high enough to insure an economical fermentation. Orange juice is rather adaptable to vinegar fermentation, because of its high sugar content, but a mixture of all citrus juices does not give the desired results.

Citric Acid

Citric acid is now produced in such large quantities that imports from Spain and Italy are no longer necessary. Calcium citrate is its by-product. The high content in citric acid of lemon makes this fruit the main raw material for the commercial production of citric acid and calcium citrate.

Pectin

Pectin, often precipitated as calcium pectate, is widely used in the manufacture of jellies. It is also used as an emulsifying agent in mineral and vegetable oils, and as a creaming agent for rubber latex. The precipitation of pectin previous to other operations, facilitates the dehydration of citrus waste.

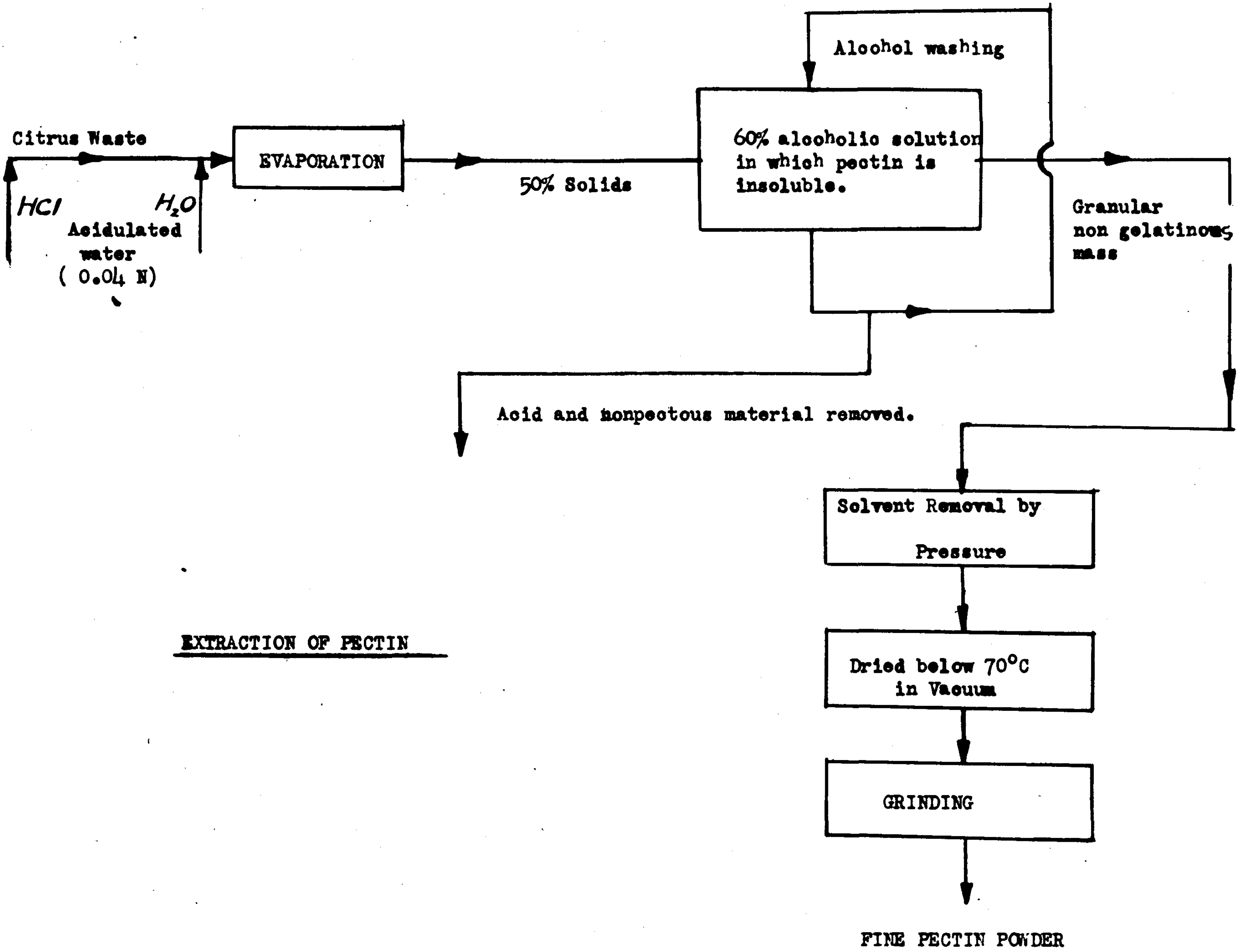

Fig. 8. Flow Sheet of the Extraction of Pectin from Citrus Waste

The apple is today's main raw material for the commercial production of pectin; nevertheless, by looking at Table VI it is evident that the amount of pectin present in citrus fruits justifies its commercial extraction. A flow sheet for such process is shown in Figure 8.

Cattle Feed

Dehydrated waste for cattlefeed has been produced on a large commercial scale for quite some time. The citrus waste is limed and pressed (13,14), the solid portion being separated from the juice by means of screen and afterwards dried on rotary driers.

It was thought at first that citrus waste feed produced a certain bitterness in milk from cows fed on such diet. It was found that naringin was the citrus constituent that produced such bitterness; therefore, its removal improved the qualities of citrus waste.

Various researchers (11) now report that citrus waste has the same feeding qualities as beets when fed to cattle; it is also cheaper.

The usefulness of citrus waste as a feed is better understood by observing in Table VIII its high digestible food value as compared with that of other commercial cattlefeed.

It is a good investment in wartime to use dehydrated citrus waste for cattlefeed in view of the cost involved in disposing of it as a sewage.

TABLE VIII

ANALYSIS OF DIGESTIBLE CONSTITUENTS OF CITRUS FRUITS (24)*

Material	Total Dry Matter	Crude Protein %	Carbohydrates %	Fat %	Total %
Common Barley	90.7	9.0	66.8	1.6	79.4
Dried Orange Pulp	87.5	6.0	70.4	0.8	78.4
Dried Lemon Pulp	92.9	3.0	69.1	0.3	72.8
Dried Beet Pulp	91.8	4.6	65.2	0.8	71.6

*Comparison between citrus wastes and two commercial cattle-feed.

TABLE IX

ANALYSIS OF WHOLE AIR-DRIED GRAPEFRUIT SEEDS AND HULLS (16)

	Seeds %	Hulls %
Moisture	11.86	10.19
Crude Fat (Ether Ext.)	30.30	1.17
Protein (N.6.25)	15.94	4.00
Crude Fiber	9.14	39.75
Nitrogen Free Ext.	30.28	-
Cellulose	-	32.50
Pentosans	-	16.34
SiO_2	0.28	-
Iron and Al_2O_3 plus Al and Fe_2O_3	0.50	-
Ca	0.36	-
Phosphates (P_2O_5)	0.56	-
Na	0.052	-
K	0.54	-

Fertilizer

The last and least important by the economical viewpoint is the use of citrus waste as a fertilizer (Table IX). It has been found that 50% of the mineral constituents of orange pulp are potash salts, 20% calcium salts, 10% phosphates, and 5% magnesium salts. Sulfur, sodium, silicon, and chlorine are present in smaller amounts (25). The presence of iron, manganese, copper, and zinc has also been reported. It has been estimated that iodine and boron are present in very minute quantities.

Shortcomings and Possibilities of Citrus Waste

The effluent discarded by the citrus by-products plants is still a cause of worry for the citrus industry because of its abnormal B.O.D. Chemical treatment is now the only method used to cope with such a public nuisance; a more thorough industrial use of citrus waste would tend to decrease the B.O.D. of such material to such a value that it could be disposed of as an ordinary sewage by the Public Utilities.

A more thorough industrial investigation of citrus waste utilization should include a research on the possibility of producing a breakfast food from the solid portion of the waste. A solvent extraction of the pulp, with different solvents, accompanied by a modern system of solvent recovery might furnish an easy method of producing some new by-products. Further research should be conducted on the production of carbon black from the dried waste. These are a few suggestions for an economic utilization of a waste that might furnish in the future an ample supply of useful by-products rather than being eliminated as an unhealthy nuisance.

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ETHYL CELLULOSE LACQUERS FOR PLASTIC COATING

and

AUTOMOTIVE ETHYL CELLULOSE LACQUERS

HISTORICAL

One of the first descriptions of ethyl cellulose and methods for its preparation appeared in 1905 in the Monatshefte fur Chemie by Suida (8), Leuchs (5), Lilienfield (16), Dreyfus (3), and many others obtained patents on the preparation of the ether. Denham (4) and his coworkers had shown that the cellulose ethers could be formed by the substitution of an alkyl or aryl radical in place of a hydroxyl hydrogen atom in cellulose. The high cost of manufacturing the ethers at that time, overcame the many industrial possibilities that were indicated. Nevertheless, a quarter of a century of active development followed, most of which is described only in patent literature (9). During this period ethyl cellulose was produced on a small scale in Germany.

Until 1936, all ethyl cellulose used in the United States was imported, but now commercial ethyl cellulose made by American manufacturers is on the market at a lower cost than the imported material. It is manufactured from cellulose, caustic soda, and ethyl chloride. Purified cellulose, whether from cotton linters or from wood pulp, is converted to alkali cellulose by treating it with concentrated caustic soda. The uniformity of treatment and the ratios of caustic soda and of water to cellulose are very carefully controlled, since these factors largely determine the degree of ethylation and the uniformity of behavior of ethyl cellulose in solvents.

The alkali cellulose is reacted with ethyl chloride in autoclaves until the desired ethoxy content and solubility are obtained. The reaction mass is treated to recover unreacted ethyl chloride and solvent by-products. The ethyl cellulose is precipitated by hot water as fine porous granules which are then washed free of salt and dried.

The two main American manufacturers of ethyl cellulose are: Dow Chemical Company, Midland, Michigan and Hercules Powder Company, Wilmington, Delaware.

THEORETICAL

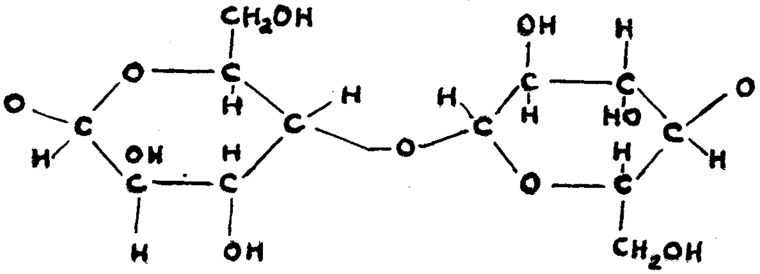
Ethyl Cellulose

Ethyl Cellulose is a cellulose ether made by the reaction of ethyl chloride with alkali cellulose, as expressed by the type reaction

$$RO(Na+Cl)C_2H_5 \rightarrow ROC_2H_5 + NaCl$$

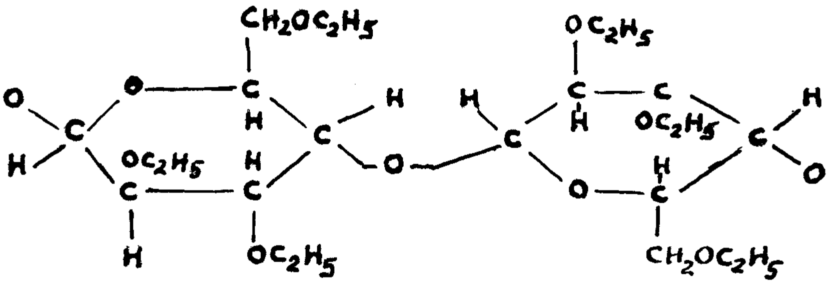
where R represents the cellulose radical (4).

The structure that is most widely accepted for the cellulose molecule is a chain of anhydro-glucose or cellobiose units linked together by oxygen bridges.



These long oxygen-linked, anhydro-glucose unit chains have great strength which is passed on to its derivatives, such as nitrocellulose, cellulose acetate, and ethyl cellulose. The properties of flexibility and toughness in these derivatives are directly attributable to this long chain structure.

From this formula it is seen that each glucose unit has three replaceable OH groups, all or part of which may react as indicated in the reaction cited above. Complete substitution of all three hydroxyl groups would give the triethyl compound, possessing a substitution value of 3, or 54.88% ethoxyl, which is illustrated in the next formula.



The completely substituted triethyl cellulose has no commercial significance, however, because it lacks strength and flexibility, is not thermoplastic, and shows extremely limited compatibility and solubility. The commercial product which exhibits the remarkable combination of useful properties, has a substitution between 2.15 and 2.60 ethoxyl groups per glucose unit, or 43 to 50% ethoxyl content.

Ethyl cellulose is a white solid resembling cellulose acetate in its flame resistance and resembling nitrocellulose in its compatibility with other film-forming ingredients.

Ethyl cellulose is practically colorless and as such it is not affected by sunlight or ultraviolet light. Accurate color control can be obtained through the use of dyes and pigments.

Ethyl cellulose is compatible with an unusually wide range of resins and plasticizers including oils and waxes.

The low density of ethyl cellulose makes it possible to get greater coverage and greater volume per unit weight than with the other cellulose derivatives. It has 45% greater coverage than nitrocellulose and 20% greater than cellulose acetate in coatings.

The excellent electrical properties of ethyl cellulose combined with its good thermal stability and outstanding flexibility and toughness led to its early and continuous use in cable lacquers where unusual conditions are encountered. Its retention of flexibility at very low temperatures is especially notable, for many compositions remain flexible even at - 70°C.

Ethyl cellulose offers no fire hazard. Its flammability is of as low an order as any other cellulosic material. If held in an open flame it will catch fire and burn, but its formulation may be made fire-resistant by the use of plasticizers and other flame-proofing agents.

The softening point of ethyl cellulose is relatively low and can be made lower by proper adjustment of plasticizers.

Other important physical properties of ethyl cellulose are its solubility in a wide variety of solvents; its stability of chemicals, which is superior to other cellulosic materials; water resistance; stability to heat; toughness. These properties make ethyl cellulose a raw material suitable for formulation of lacquer.

A lacquer is a protective coating with the following constituents: cellulose, resin, pigment, plasticizer, diluent, and solvent. Pigment may or may not be present. The first four constituents represent the non-volatile portion, while the last two represent the volatile portion.

Hardening and film formation in lacquers are dependent primarily on solvent evaporation and to a much lesser extent on the oxidation and polymerization of any oxidizing alkyds or similar materials that might be present. The relative amount of ethyl cellulose has a definite influence on the drying rate of the lacquer film and on its toughness: the greater the relative amount of ethyl cellulose the greater the drying rate and the toughness. A higher amount of hard resin increases the glossy properties of the film surface and makes it short. Plasticizers are used to increase the flexibility.

Solvents are used to dissolve the cellulose and to decrease the viscosity of the lacquer so that it can be either brushed or sprayed.

All the lacquer constituents are thoroughly mixed by different methods and different pieces of equipment, eg., 2, 3, 4, 5 roll mills, ball mill, roller mixer, and Banbury mixer. Chips can also be prepared by grinding and mixing cellulose, pigment, and solvent through a roll mill; this method facilitates the handling of pigment and reduces the total grinding time.

ETHYL CELLULOSE FOR PLASTIC COATING

INTRODUCTION

Ethyl cellulose plastic is well known as a thermoplastic molding compound, being an ether of ethyl alcohol and cellulose. It is outstanding in touchness and strength, shock resistance at low temperature, and retention of original properties on aging or on exposure to a wide range of temperature-humidity conditions. It is available in various forms for extrusion, compression, or injection molding as well as a variety of flow grades.

This plastic can be manufactured in transparent forms and can be pigmented to a wide range of coloration. The use of a lacquer for surface coloration is sometimes more advisable to cover slight imperfections which might appear in the extruded or molded product; the gloss is also improved and the range of low gloss plastic coloration is wide.

The choice of a suitable lacquer involves a thorough study of solvent to be used for thinning and spraying. Some solvents (2,4) cannot be used satisfactorily because they make the surface of the plastic mushy with a consequent rough appearance of the lacquer film. Strong solvents produce warping of the thin plastic sections.

It was decided to develop a cheap white ethyl cellulose lacquer to be used as a protective coating of thin plastic sections and having as its characteristics high gloss, hardness, flexibility, and a durability similar to that of the ethyl cellulose plastics. Different resins were used to generalize the final formulation; a cheap solvent line-up was also investigated.

EXPERIMENTAL

Equipment

A two-roll mill, a ball mill, and a roller mixer were used for the dispersion of the pigmented lacquer. The lacquer was sprayed on 6" ethocel plastic discs with a spraying gun. An accelerated weathering unit, National Carbon Company type with Corex D filters for Sunshine rays was used for accelerated weathering treatment.

Procedure and Results

The first step was to obtain a two-roll mill dispersion of the pigment in ethyl cellulose. A mix of 53.3% Titanium Dioxide, 38.7% Ethyl Cellulose, and 8.0% n-Butanol bay weight was made and ground on a differential speed two-roll mill for 15 minutes. The butanol was added to gel the ethyl cellulose so that the mass would adhere to the roll for a sufficient length of time for the ethyl cellulose to become plastic because of the increase of temperature caused by milling. Because of the volatility of butanol the composition of the chips was assumed to be:

Titanium Dioxide (Kreb's R-110)	56.7%
Ethocel, 7 cps. Std. Ethoxy	41.3%
n-Butanol	2.0%
Total	100.0%

This assumption was made on the basis of many similar grinds for industrial application, where titanium dioxide and similar pigments that permit a high pigment to resin ratio would give a chip at 98% non-volatile; ferrite and similar pigments give chips at 95% N.V., and the organic colors, blacks, and blue chips at 98% N.V.

These chips were blended with the desired amounts of other constituents by mixing them in round pint cans which rolled for 12 hours.

The first lacquer PL-1 (Table X) that was tried had a good flexibility and hardness when sprayed on tin panels, but, when sprayed on the ethyl cellulose plastic discs, a soft rough film resulted. It was thought that this was caused by the bleeding of the die lubricant from the plastics into the lacquer film. It was therefore decided to decrease the plasticizer and to increase the hard resin, because the die lubricant had the effect of increasing the apparent percentage of plasticizer present in the lacquer.

For a preliminary work, combinations of different hard resins and ethyl cellulose percentages, without the use of plasticizer, were investigated, with the idea in mind of selecting the best resin and afterwards use it with different amounts of plasticizers to find an optimum percentage of plasticizer.

TABLE X

LACQUER FORMULATIONS

	PL-1	PL-2	PL-3	PL-4	PL-5
% Pigment Krebs RT-110	6.50	8.50	8.50	8.50	8.50
% Ethocel 10 cps. Std.	13.00	6.20	6.20	6.20	6.20
% Beckacite 3000	-	31.10	-	-	-
% Amberol M-93	-	-	31.10	-	-
% Beckacite 1113	-	-	-	31.10	-
% Syntex H-3	1.20	-	-	-	31.20
% Congo	-	-	-	-	-
% Undewaxed Dammar	-	-	-	-	-
% Beckosol 1324	1.70	-	-	-	-
% Amberlac B-94	3.00	-	-	-	-
% Dow Plasticizer No. 6	10.00	-	-	-	-
% Total Solvent	64.60	54.20	54.20	54.20	54.20
% n-Butanol	-	-	-	-	-
% Industrial Xylol	-	-	-	-	-
% Shell TS-28	-	-	-	-	-

TABLE X

(Continued)

	PL-6	PL-7	Pl-8	PL-9	PL-10
% Pigment Krebs RT-110	8.50	8.50	7.73	7.73	7.73
% Ethocel 10 cps. Std.	6.20	6.20	14.73	5.63	7.90
% Beckacite 3000	-	-	-	-	-
% Amberol M-93	-	-	-	-	-
% Beckacite 1113	-	-	-	-	-
% Syntex H-3	-	-	-	28.26	21.21
% Congo	31.20	-	-	-	-
% Undewaxed Dammar	-	31.20	-	-	-
% Beckosol 1324	-	-	-	-	-
% Amberlac B-94	-	-	-	-	-
% Dow Plasticizer No. 6	-	-	9.10	9.10	9.10
% Total Solvent	54.20	54.20	-	-	-
% n-Butanol	-	-	6.62	6.08	6.22
% Industrial Xylol	-	-	27.30	27.30	27.30
% Shell TS-28	-	-	34.52	15.90	20.55

Two types of unmodified phenolic resins were used - Amberol M-93 and Beckacite 3000, a modified phenolic Beckacite 1113, a maleic modified ester gum Syntex H-3, and two natural resins Congo and undewaxed Dammar. Pure Ester Gum was not used because of its poor solvent release.

These lacquers were reduced in the ratio of two volumes of lacquer to one volume of thinner which was a mixture of 50% Solvesso No. 1, 30% Xylol, and 20% Butanol.

Two coats were sprayed on the ethyl cellulose discs, and the lacquer film was air dried for several days; it was afterwards submitted to accelerated weathering for 50 hours. The results obtained are shown in Table XI. From these it appears that Syntex H-3 is among the best beside being the least expensive. Various other maleic estergums were tried with the same results.

The discs used in further work were thinner and softer than those previously used, they were green in color; the lacquer film sprayed on them was not uniform and lacked gloss; this was probably due to incompatibility of the die lubricant with the lacquer. It was found that by polishing on a metallurgical wheel it was possible to remove such inconvenience.

In order to prevent shortness of film and warping of the thin plastic discs, a series of lacquers with three different plasticizers at various ratios were prepared.

One, two, four, and ten per cent dibutyl phthalate, blown castor oil, and Dow P-6 plasticizer (di-monophenyl phosphate) were added to PL-5. The addition of 4% of blown castor oil produced films that were too soft, but 4% of the other plasticizers was not sufficient to stabilize the surface pull. The lacquer with 10% Dow P-6 gave a film with good hardness and a minimum amount of curling, but, after accelerated weathering treatment, bad cracking occurred. This was probably caused by the low ratio of ethyl cellulose to hard resin, the latter contributing to the formation of a non-flexible film.

Two lacquers were prepared, one with 9.1% Dow P-6 on PL-5 formulation, the other similar but using cellulose without resin. These new formulations were called PL-8 and PL-9 respectively.

These two lacquers were blended in ratios of three to one, one to one, and one to three, reduced, and sprayed on thin green plastic discs using Lacquer PL-9 as the standard. After 60 hours of accelerated weathering treatment, Lacquer PL-9 cracked and curled badly. The others were in good condition and with increased gloss because of the higher ratios of ethyl cellulose. This factor, together with the higher cost, indicated that the one to three ratio was the best and this new formulation was called PL-10.

TABLE XI

ACCELERATED WEATHERING FOR 50 CYCLES

Lacquer	Resin	Results after 50 hours
PL-2	Beckacite 3000	Bad cracking and yellowing
PL-3	Amberol M-93	Bad initial cracking; yellow; low gloss
PL-4	Beckacite 1113	Slight cracking, more yellow than H-3
PL-5	Syntex H-3	Slight cracking, fairly good color
PL-6	Congo	Initial color yellow, loss of gloss
PL-7	Undewaxed Dammar	Very bad cracking, loss of gloss

All troubles with flat and low gloss spots disappeared when the amount of ethyl cellulose was increased, the die lubricant or plasticizer being more compatible with ethyl cellulose than with the hard resin.

At this stage of the research it was decided to try several other hard resins in place of Syntex H-3. Several other maleic ester gum resins were substituted, namely Amberol 800, Teglac 152, Teglac Z-152, Teglac 161, and Beckacite 1110. Amberol 800 gave a wrinkled appearance to the film; Beckacite originally gave a uniform film, but on exposure to ultraviolet light it tended to wrinkle. All of the Teglac resins gave very good results.

To lower the cost of lacquer and also to decrease still further the curling tendency of the panels when placed in the accelerated weathering machine, several formulations were made using VM&P naphtha instead of xylol and reducing the amount of alcohol.

It was found that reducing the amount of butanol caused the reappearance of pin holes, and further reduction resulted in a solvent too weak to dissolve the ethyl cellulose. However, replacement of xylol with VM&P gave good results.

To check whether the warpage of the panels was due to solvent action or to the effect of heat, coated panels together with uncoated panels were placed in the weatherometer. The results showed that the bare panels warped as badly as, if not worse than the lacquered panels. This showed that heat had more influence on the warping of the panels than the solvent present in the lacquer. A further increase in amount of Dow No. 6 plasticizer was effected to decrease the surface pull, but this increase resulted in softer films, and because of its high cost, a return to the 9.1% figure was made.

It was also noted that the panels coated with lacquer curled only in one direction with a definite concave surface and angle of curvature, while the untreated panels curled in such a way as to present a wavy appearance with several concave and convex surfaces and different angles of curvature.

CONCLUSION

The results obtained show that a good formulation for a white lacquer to be used on ethyl cellulose molded plastic is:

Titanium Dioxide (Krebs RT-110)	Two roll mill chip	7.72%
7 cps. Ethocel (Std. Ethoxy)		5.63%
n-Butanol		0.27%
		13.62%
7 cps. Ethocel (Std. Ethoxy)		2.27%
Maleic Resins or Teglac Resins		21.21%
Dow P-6		9.10%
n-Butanol		5.95%
Shell TS-28		20.55%
		100.00%

Different pigments can be used with equal results; the percentage of the pigment might have to be varied in accordance with its hiding power.

The spraying solvent should be mixed with the lacquer in the ratio one to two and should be composed of 50% Solvesso No. 1, 30% industrial Xylol, and 20% n-Butanol. It is important to stress that the amount of n-Butanol used in the formulation of the lacquer and the spraying solvent, is strictly a minimum; a lesser amount would cause pin holing in the lacquer film because of incomplete solution of the ethyl cellulose in the solvent.

ETHYL CELLULOSE AUTOMOTIVE LACQUER

INTRODUCTION

Ethyl Cellulose, with its unusual combination of properties, is one of the most versatile of the cellulose derivatives. Its advantages are flame stability and compatibility with petroleum thinners to an extent unusually high for cellulose derivatives. Its disadvantages are softness and incompatibility with a large number of resins.

The research was concerned with the development of a surfacer and a top coat for the Automobile Industry. Previous work had been done in this particular field; a gray sanding surfacer and a black top coat had already been developed. The purpose was to investigate the versatility of the two formulations, i.e., coloration and compatibility of ethyl cellulose with cheap resins and solvents. The improvement of the physical properties of the two original lacquers was also the object of this investigation.

EXPERIMENTAL

Equipment:

A two-roll mill, a ball mill, and a roller mixer were used for the dispersion of the pigmented lacquer.

The lacquer was sprayed on standard 20 gauge 3½" x 7" and 5" x 10" steel panels.

An accelerated weathering unit, National Carbon Company type, with Corex D filters for Sunshine Carbons, was used for accelerated weathering.

Procedure and Results:

The first part of the investigation was to generalize the standard formulations for Gray Surfacer (Table XIII) by substituting different resins for Super Beckacite 3000 which is rather expensive and using different solvent ratios. The new formulations are shown in Table XIV.

These lacquers were sprayed on steel panels and air dried for two days at room temperature. No. 62-A Ethocel Black Coat was sprayed on half the surface of each panel to establish the adherence of such a top coat on the newly formulated surfacer. The panels obtained were exposed to accelerated weathering for 150 hours.

The surfacers, except No. 62 Standard Gray Sanding surfacer, failed after 50 cycles; this was caused mainly by poor pigment dispersion. The comparison standard panel failed after 100 cycles. After 150 cycles of accelerated weathering, all the top coats appeared in good condition. Tests for flexibility, hardness, and gloss were run.

The test for flexibility was run by bending each panel around a one inch steel pipe; the hardness was determined by scratching the lacquer film with different pencils held at a 45° angle and observing the maximum resistance of the lacquer to scratch. Tests for gloss were run by visual comparison. The results obtained are shown in Table XV.

It was found that ethocel was quite compatible with the different resins used and that the substitution of VM&P naphtha for part of the toluol previously used did not apparently change the uniformity and the gloss of the film.

Three typical resins were selected from those previously used to be substituted for Super Beckacite 3000 in No. 62 Gray Sanding Surfacer and in No. 62-A Black Ethocel Top Coat. The resins selected were Teglac Z-152 (modified alkyd); Beckacite 1111 (modified phenolic); Amberol 800 Ex.-Lt. (pure phenolic). Another formulation was made whereby toluol was substituted by a 50-50 mixture of toluol and VM&P naphtha with Amberol 800 Ex.-Lt. as the resin. It was also decided to spray differently pigmented topcoats, and to compare them with standard No. 62 lacquers with similar pigmentation.

TABLE XII

62-A BLACK TOP COAT

Carbon Black	5.95% RBH Dispersion No. 9002	0.893%
10 cps. Ethyl Cellulose		0.893%
Ethyl Alcohol		0.834%
Toluol		3.330%
10 cps. Ethyl Cellulose Standard Ethoxy		10.600%
Beckacite 3000		11.500%
Aroplaz 930		5.700%
Ethyl Alcohol		12.200%
Toluol		54.050%
		100.000%

TABLE XIII

62 GRAY SANDING SURFACER

Lithopone	11.62%
China Clay	4.13%
Celite ON-110	3.34%
Asbestine	4.13%
Carbon Black	4.58%
Ethyl Cellulose	4.58%
Ethyl Alcohol	4.24%
Toluol	16.90%
Beckacite 3000	8.65%
Aroplaz 930	4.32%
Ethyl Alcohol	4.83%
Toluol	24.21%
Pebble Mill Grind	
10 cps. Ethyl Cellulose Standard Ethoxy	4.47%
	100.00%

TABLE XIV

FORMULATIONS OF GRAY SANDING SURFACER

Formulation	Resin Substitution*
No. 62-A	Super Beckacite 3000
No. 62-B	Beckacite 1113
No. 62-C	Teglac 161
No. 62-D	Teglac 152
No. 62-E	Teglac Z-152
No. 62-F	Beckacite 1111
No. 62-G	Amberol F-7 Lt.
No. 62-H	Amberol 800 Ex. Lt.
No. 62-I	Amberol 801
No. 62-J	Amberol B/S-1 Lt.
	Solvent Substitution**
No. 62-O	20-44 VM&P Naphtha - Toluol
No. 62-P	40-24 VM&P Naphtha - Toluol
No. 62-Q	All VM&P Naphtha
No. 62-R	5-6.2 Mineral Spirits-Ethanol

*The resin was substituted in equal weight for Super Beckacite 3000 in the original Formula No. 62.

**The solvent was substituted in equal volume for toluol in the original Formula No. 62.

TABLE XV

PHYSICAL TESTS ON GRAY SANDING SURFACERS

Surfacer	Top Coat after 210 Cycles	Pencil Hardness	Flexibility	Gloss Retention (Comparison)
62-A	Excellent	6H	Excellent	Good
62-E	Excellent	4H	Excellent	Poor
62-O	Excellent	4H	Fair	Good
62-D	Excellent	6H	Good	Fair
62-H	Excellent	5H	Good	Good
62-G	Excellent	4H	Good	Good
62-J	Excellent	4H	Fair	Good
62-A	Excellent	4H	Bad	Good
62-C	Excellent	4H	Bad	Good
62-K	Excellent	4H	Very Brittle	Fair
62-E	Excellent	4H	Very Brittle	Poor
62-I	Excellent	4H	Bad	Fair
62-B	Excellent	3H	Bad	-

TABLE XVI

FORMULATIONS FOR GRAY SANDING SURFACERS AND COLORED TOP COATS

Surfacer	Substitution in 62*
No. 70	Teglac Z-152
No. 71	Beckacite 1111
No. 72	Amberol Ex. Lt. 800
No. 73	Amberol 800 Ex. Lt. & 50-50 Toluol-VM&P

Top Coat	Pigment	Substitution in 62-A**
No. 101	Titanium Dioxide	Amberol 800 Ex. Lt.
No. 102	Titanium Dioxide	Beckacite 1111
No. 103	Titanium Dioxide	Teglac Z-152
No. 104	Titanium Dioxide	Amberol 800 Ex. Lt. & 50-50 Toluol-VM&P
No. 111	Toluidine Red	Amberol 800 Ex. Lt.
No. 112	Toluidine Red	Beckacite 1111
No. 113	Toluidine Red	Teglac Z-152
No. 114	Toluidine Red	Amberol 800 Ex. Lt. & 50-50 Toluol-VM&P Naphtha
No. 121	Lt. Chrome Yellow	Amberol 800 Ex. Lt.
No. 122	Lt. Chrome Yellow	Beckacite 1111
No. 123	Lt. Chrome Yellow	Teglac Z-152
No. 124	Lt. Chrome Yellow	Amberol 800 Ex. Lt. 50-50 Toluol-VM&P Naphtha

*Each resin was substituted in equal weights for Super Beckacite 3000 in Formula No. 62.

**Each resin was substituted in equal weights for Super Beckacite 3000 in Formula No. 62-A.

TABLE XVI

(Continued)

Top Coat	Pigment	Substitution in 62-A
No. 131	Carbon Black	Amberol 800 Ex. Lt.
No. 132	Carbon Black	Beckacite 1111
No. 133	Carbon Black	Teglac Z-152
No. 134	Carbon Black	Amberol 800 Ex. Lt. & 50-50 Toluol-VM&P Naphtha
No. 141	Iron Blue	Amberol 800 Ex. Lt.
No. 142	Iron Blue	Beckacite 1111
No. 143	Iron Blue	Teglac Z-152
No. 144	Iron Blue	Amberol 800 Ex. Lt. & 50-50 Toluol-VM&P Naphtha
No. 151	Med. Chrome Green	Amberol 800 Ex. Lt.
No. 152	Med. Chrome Green	Beckacite 1111
No. 153	Med. Chrome Green	Teglac Z-152
No. 154	Med. Chrome Green	Amberol 800 Ex. Lt. & 50-50 Toluol-VM&P Naphtha

The pigments selected were:

Iron Blue
Titanium Dioxide
Carbon Black
Chrome Green
Chrome Yellow
Toluidine Red

These top coats were sprayed on surfacers of similar composition. Their formulations are shown in Table XVI. All these lacquers were finally compared with Rinshed-Mason equicolored nitrocellulose lacquers for weathering, hardness, and flexibility. The panels were sprayed with one coat of surfacer and two coats of top coat. They were placed in the weatherometer after having been air dried for two days at room temperature. Duplicates were prepared for physical testing.

The results obtained after 50 cycles and 150 cycles of weathering treatment are shown in Tables XVII and XVIII.

During the preparations of the above mentioned panels, it was noticed that the spraying solvent used was too volatile; the rate of evaporation was so fast that the spray was almost dry, and such condition affected the film to the point of being rough, non-uniform and of poor gloss. It was decided that in the next investigation a different spraying solvent would be investigated so that such inconveniences would be eliminated. The spraying solvent which had been used in the preliminary of the investigation was a mixture of ethanol and toluene, 30%-50% by volume.

TABLE XVII

ACCELERATED WEATHERING FOR 50 CYCLES

Surfacer	Top Coat	Remarks
62-A	124	Darkening
62-A	62 White	Yellowing
62-A	123	Darkening
71	122	Darkening
72	121	Darkening
72	101	Cracking
70	62 White	Cracking
62-A	121	Darkening
62-A	122	Darkening
73	124	Darkening
70	123	Darkening

TABLE XVIII

ACCELERATED WEATHERING FOR 150 CYCLES

Surfacer	Top Coat	Remarks
72	62 White	Cracking
RM	RM White	Good gloss retention
62	154	Stress lines
73	133	Loss of gloss
62	112	Stress lines; loss of gloss
62	131	Loss of gloss
62	111	Loss of gloss
RM Gray	RM Red	Loss of gloss
70	113	Loss of gloss
62	152	Some blistering; gloss retention
72	62-A Black	Loss of gloss
71	132	Loss of gloss
62	124	Darkening; stress lines; cracking; some peeling
62	114	Stress lines; loss of gloss
73	144	Stress lines; loss of gloss
70	134	Loss of gloss
62	123	Darkening; stress lines
62	151	Cracking; stress lines; loss of gloss
RM Gray	RM-Green	Loss of Gloss
62	132	Loss of Gloss
62	103	Some cracking

TABLE XVIII

(Continued)

Surfacer	Top Coat	Remarks
70	143	Some stress lines
RM Gray	RM Black	Loss of gloss; fading
62	62-A Green	Gloss retention
72	62-A Green	Stress lines
72	112	Few stress lines; loss of gloss
62	62-A White	Yellowing
62	133	Loss of gloss
70	62-A White	Cracking and peeling
62	144	Few stress lines
RM	RM Blue	Gloss retention
62	121	Darkening and cracking
62	134	Loss of gloss
72	121	Darkening and cracking
70	62 Green	Few stress lines
73	124	Darkening; stress lines; cracking
62	153	Few stress lines; some gloss retention
72	141	Stress lines
62	104	Cracking; peeling
62	122	Darkening; gloss retention

TABLE XVIII

(Continued)

Surfacer	Top Coat	Remarks
71	62-A Green	Good gloss retention
70	123	Darkening; cracking; peeling
62	113	Few stress lines; loss of gloss
62	141	Some gloss retention
71	122	Some gloss retention; little darkening effect
62	62-A Black	Loss of gloss
62	62-A Blue	Gloss retention
71	111	Loss of gloss
RM Gray	RM Yellow	Some gloss retention
62	102	Some cracking
62	101	Cracking; peeling
71	62-A White	Cracking; peeling
70	114	Stress lines; loss of gloss
73	62-A Green	Stress lines; cracking
62	62-A Blue	Gloss retention
70	143	Few stress lines; gloss retention
62	142	Gloss retention

The surfacers showed very good weather stability, definitely proving that a previous failure was caused by poor dispersion of pigment.

In the case of the lighter colors, it was noticed that a higher pigment ratio was necessary to obtain better covering power. Especially the Chrome Yellow showed so poor a hiding power that even two coats were not sufficient for a definite covering of the surfacer.

The flexibility test showed that all the surfacers were very flexible and conserved their flexibility even after weathering. The top coats compared favorably with the Rinshed-Mason nitrocellulose top coats before weathering, but had lost their flexibility after such test while the Rinshed-Mason lacquers had not been affected.

The results obtained showed that chips whose composition is shown in Tables XIX and XX, were not very satisfactory for dispersion and gloss; therefore it was decided to use RBH dispersions for the further development of the gray sanding surfacer and colored top coats. The composition of these ethyl cellulose RBH dispersions is shown in Table XXI.

The new surfacer developed differed from the previous ones only in that RBH dispersions were used instead of ethyl cellulose chips. Different percentages of plasticizers were investigated. Dow P-6, which is a di-monophenyl phosphate,

TABLE XIX

CHIP COMPOSITION BEFORE MILLING

Pigment	% Pig.	% E/C	% Aroplaz 930	% Butanol
Lt. Chrome Yellow	53.3	38.7	-	8.0
Med. Chrome Green	53.3	38.7	-	8.0
Ferrite Yellow	53.3	38.7	-	8.0
Ferrite Red	53.3	38.7	-	8.0
Titanium Dioxide	53.3	38.7	-	8.0
Iron Blue	36.7	36.7	11.6	15.0
Lampblack	34.8	34.8	17.4	13.0
Carbon Black	34.8	34.8	17.4	13.0
Toluidine Red	53.3	38.7	-	8.0

TABLE XX

CHIP COMPOSITION AFTER MILLING*

Pigment	% Pig.	% E/C	% Aroplaz 930	% Butanol
Lt. Chrome Yellow	55.0	40.0	-	5.0
Med. Chrome Green	55.0	40.0	-	5.0
Ferrite Yellow	55.0	40.0	-	5.0
Ferrite Red	55.0	40.0	-	5.0
Titanium Dioxide	56.7	41.3	-	2.0
Iron Blue	39.7	39.7	12.6	8.0
Lamp Black	36.8	36.8	18.4	8.0
Carbon Black	36.8	36.8	18.4	8.0
Toluidine Red	55.0	40.0	-	5.0

*Calculated percentages

TABLE XXI

RBH ETHYL CELLULOSE PASTES

Color	% Pigment	% 18-20 cps. Ethyl Cellulose	% Ethyl Alcohol	% Toluol	% Dibutyl Phthalate
Titanium Dioxide	50.00	7.00	8.50	34.50	-
Carbon Black	15.00	15.00	14.00	56.00	-
Toluidine Red	18.00	14.50	31.90	32.00	3.60
Iron Blue	15.00	15.00	34.25	34.25	1.50
Chrome Green Medium Deep	25.00	9.40	13.00	52.60	-
Primrose Chrome Yellow	56.00	8.00	7.50	28.50	-

was substituted for Aroplaz 930 in some of the formulations to see whether it was possible to obtain more flexibility in the lacquer film. Aroplaz 930, an alkyd-non-oxidizing resin, is not classified as a plasticizer although it acts as such.

The results showed that no apparent change in the characteristics of the surfacer was visible when different percentages of plasticizers were used up to 7%. The panels were baked at 212°F. for 3 hours and at 300°F. for 5 hours, then they were tested for flexibility and adhesion. None of them failed.

During the surfacer investigation it was found that, because of its slower evaporation rate, a 30-70 Ethanol-Xylene mixture was a better spraying solvent than 30-70 Ethanol-Toluene.

To continue in the development of a top coat, an RBH toluidine red pigmented top coat was prepared with different percentages of plasticizer. It was found that a 30-70 Ethanol-Xylene mixture did not thin it to a consistency suitable for spraying, because Xylene is a diluent, not a solvent, and as such, its evaporation is not consistent with that of Ethanol, producing pin points in the lacquer film after drying. In the case of surfacers, such inconvenience was not experienced because of the presence of inert materials which make the surface of a bottom coat rather rough.

The use of a better spraying solvent was necessary. It was found that two solvent mixtures were particularly propitious, i.e., 60-20-20 Xylol, Butanol and Isopropyl Alcohol or 60-25-15 Xylol, Butanol and Ethanol. Three thin coats of red ethyl cellulose lacquer were sprayed, by using such solvent mixtures as spraying solvents, and the resulting films were glossy and smooth; they dried in seven minutes to tack free, and they did not show any sagging or orange peeling. The panels were tested for flexibility, and good results were obtained even when the original percentage of plasticizer was used.

CONCLUSION

It can be concluded that the original formulations 62 and 62-A for a gray sanding surfacer and a black top coat respectively are good. Their versatility has been proved by substituting for Super Beckacite 3000 several Teglacs, Beckacites and Amberols, achieving equal success.

Investigation on different pigmentations has shown that the pigment-vehicle ratio is too low especially in the case of the lighter shades. An increase in pigment should be made depending on the hiding power of the pigment.

The surfacer and top coat should be thinned with a solvent which evaporates fairly fast and uniformly. Two solvent formulations are advised: 60-20-20 Xylol-Butanol-Isopropyl Alcohol or 60-25-15 Xylol-Butanol-Ethanol.

In the formulation of the top coats a 50-50 mixture of VM&P Naphtha and Toluol can satisfactorily substitute Toluol.

The adhesion of the top coat to the surfacer is so good that in no case was it possible to separate them. The flexibility of the top coat should be further investigated; tests have shown that the surface pull of the top coat is greater than that of the surfacer, thereby creating such stresses on the bottom coat that on bending the panels, the surfacer is pulled off the base metal.

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VITA

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