THE RECOVERY OF ACETIC ACID FROM WASTES OF TANNING EXTRACT MANUFACTURE

by

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TABLE OF CONTENTS

INTRODUCTION

Tanning materials are obtained from leaves, bark, wood, and roots of a number of plants. In 1939 the tanning extract industry marketed roughly three million gallons of tanning extract. Although the industry is not a large one, it has problems of waste disposal and utilization.

Two general steps are necessary to obtain tanning materials: the extraction proper, and concentration of the resulting thin liquor extract. Problems encountered performing these overall steps are: disposition of the spent chips by burning in boilers with special grate surfaces; separation of non-tannin insoluble constituents from tannin solutions; disposal of large volumes of vapor condensate during concentration of the extract. The condensate contains roughly 0.02-0.5% acetic acid and represents a recoverable waste. Removal of the acid from the condensate would permit the use of the water elsewhere in the manufacturing process. In the condensate minute amounts of pyroligneous acid, tarry oils, and creosotes are also present. The nature of the condensate as a whole is a clear to pale yellow solution with very little suspended matter.

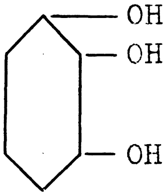
Adams and Holmes in 1934 were successful in removing acetic acid from dilute solutions by employing synthetic resin ion exchange materials, but no quantitative results were obtained. Other attempts have been made to recover acetic acid by liquid-liquid extraction, azeotropic distillation, and other methods not described but these methods have been impractical when handling low concentrations due to costs involved.

The purpose of this investigation is to recover acetic acid from the wastes of the tanning extract industry. Primary consideration will be given processes dealing with ion exchange materials.

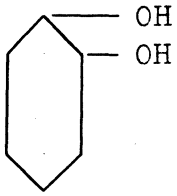
II. REVIEW OF LITERATURE

A. TANNINS

Probably the most comprehensive study of tannins to date has been made by Harvey(11) in 1921. According to him, tannins are a group of similar astringent substances occurring in various parts of plants, i.e., leaves, bark, wood, roots, etc. The classification of tannins for technical purposes is based on the decomposition products formed by the action of heat. In the main, one of two substances is formed, pyrogallol or catechol:



Pyrogallol



Catechol

Sources. The catechol tannins are obtained from birch bark, oak bark, quebracho, mangrove, ulmo, gambier, mimosa bark, hemlock, mallet bark, lentisco, and pine bark. The pyrogallol tannins are obtained from myrobalams, valonia, algarabilla, oakwood, galls, chestnut wood, willow bark, sumach, and babool. Chestnut wood, producing the pyrogallol tannin, is most frequently used in this region and subsequent discussion will be focused mainly on chestnut wood extract.

Uses of Tannins. Tannins are used extensively in the manufacture of leather from hides. It is often desirable to prepare tanning solutions consisting of mixed tannins in order to produce leathers of varying types, possessing different qualities of softness, finish, and color. Other less important uses(9), from the standpoint of tannin volume consumed, include protective colloids, photography, dyes, intermediates, medicines, and analytical reagents.

B. MANUFACTURE OF TANNING EXTRACT

Tanning extract is manufactured at a number of plants all over the country(8). Plant sites are chosen primarily on the basis of a large supply of suitable materials for extraction and on the basis of an iron-free supply of water(11). Soft water is advantageous and numerous methods are employed to treat raw waters to remove hardness.

Extraction. Before the tannin can be extracted, the material must first be reduced to the proper size essential for thorough extraction, and for this purpose, crushers, chippers, etc., are employed according to the nature of the raw material(11). This process, in the case of chestnut wood, consists of reducing the 5-foot logs to chips in rotary, multiblade, chipping machines. The idea of chipping is to open the ends of the material(11). The chestnut chips are passed through a swing-hammer mill, or some other device of similar action, to shred the chips allowing for greater penetration of the chips by the extracting solvent. The finer the material, the better the extraction, although too fine material must be avoided to prevent clogging of the leachers(11).

The extraction of the tannin from the ground material may be carried out by a number of processes(11), thus:

(1) Open vat extraction

(2) Rotary system

(3) Pressure autoclaves

(4) Oven vat with Archimedian screw

(5) Vacuum extraction (Nance process)

(6) Roller extraction

(7) Gas lift agitation method

Extraction(11) of chipped chestnut wood is made either in open vats of wood or copper, or under pressure in autoclaves, and although many factories use the latter process, the open vat system is considered the better of the two. Under pressure, more non-tannin substances are extracted and a certain loss of tannin occurs; thus, although the total yield of extract is greater, the quality is inferior to that made by open vat extraction.

In either open vat extraction or pressure autoclaves, the extraction is usually carried out by countercurrent flow, i.e., the solvent entering the system first passes into the vat or autoclave which is most nearly spent and passes through successively richer chips until it leaves the system from the charge which has been leached the least. Water is universally used as the solvent. Upon leaving the extraction vats, the liquor should contain up to 10-11 percent of dissolved solids, the tannin content, of course, varying with the composition of the raw material(11).

<u>Clarification</u> <u>and</u> <u>Decoloration</u>. The weak liquor from the extractors must be clarified, and if necessary decolorized. The liquor is

pumped into large settling tanks and there decolorized by chemical means, and then filtered. A few of the decolorizing agents are the following: oxalic acid, gelatinous alumina, albumin-containing substances (e.g. ox blood), and lead carbonate followed by lead sulphate(11).

Filtration can be done by any one of the following processes:

(1) Simple sedimentation

(2) With filter cloths over wooden frames

(3) By filter presses

(4) By centrifuging

Sedimentation is sometimes accelerated by concentration of the weak liquor to a specific gravity of 1.06 in evaporators, then allowing it to stand.

Evaporation. The liquor, after clarification, is then concentrated in order to remove the greater part of the water. Use of open pans for concentration is not advisable due to high temperatures causing decomposition of the tannin in solution(11). In order to secure a low temperature at the correct stage of the evaporation process, vacuum evaporators are adopted. The single effect evaporator may be used but more economical operation is obtained using a multiple effect evaporator(11). The product is usually concentrated to 25 or 35 percent tannin.

Some leather manufacturers prefer powdered extract, in which case the 35 percent tannin solutions are dried on heated rolls (130°F.) under vacuum conditions. The time necessary for drying to a moisture content of 3 percent is 7 to 8 seconds(19). No damage to the extract occurs in this short time at 130°F.(19).

During evaporation, the vapors driven off are largely composed of water but small amounts of acetic acid are present. Gonzalez(8) states that the water driven off during concentration of the extract contains "from one-half to two percent acetic acid". This appears to be high since two tannin extract manufacturers, Leas & McVitty, Inc.(29), of Salem, Virginia, and the Mead Corporation(25), Tannin Extract Division, of Lynchburg, Virginia, concur in reporting 0.03 percent total acids expressed as acetic acid.

C. ION EXCHANGE

Ion exchange is becoming increasingly important in industry and therefore is receiving increasing attention as a subject of laboratory study. Many investigations have been made of the various phases of ion exchange but surprisingly few unquestionable facts have been extended.

Walton(28) defines ion exchange as a "reversible interchange of ions between a liquid phase and a solid body which does not involve any radical change in the solid structure." When the exchange involves positively charged ions (cations) it is called base-exchange or cation exchange. Exchange between negatively charged ions (anions) is known as anion exchange.

Even such a definition as Walton gives above, while quite broad, is not above attack since the term "ion exchange" is also applied to adsorption of whole molecules from solutions as in the case of free acids. This acid adsorbing property of some ion exchange materials makes it worthwhile to investigate the possibilities of utilizing them to recover acetic acid from wastes of tanning extract manufacture.

<u>History</u>. The phenomena of base-exchange was first observed by Way(18), in 1850, when he passed a solution of potassium chloride through a bed of soil, and found that all potassium was removed from the solution and replaced by an equivalent amount of calcium and sodium from the soil. Eichorn(18) discovered that bases were mutually exchangeable. Lember, Eichorn, and Gans studied the mineral exchangers exhaustively, and later Gans made the first commercial applications of zeolites to softening water. In 1935, Adams and Holmes(1) discovered that phenol-formaldehyde resins exhibited ion exchange properties, especially anion exchange when certain derivatives were used, and in so doing opened a new era in the chemistry of synthetic resins and applications of the ion exchange principle. The further development of synthetic resins as ion-exchangers has been investigated in the laboratories of the I.G. Farbenindustrie and the Resinous Products and Chemical Company, who are licensees under the Holmes(1) patents in Europe and in the United States respectively. The Permutit Company has also conducted extensive research concerning ion exchange.

<u>Classification of Ion Exchangers</u>. No general classification of exchange adsorbents appears to have been made. However, the following has been suggested(18):

I. Cation-Exchange Adsorbents
  A. Inorganic
    1. Natural origin
      a. Unmodified (example, natural greensand)
      b. Modified (example, fortified greensand)
    2. Synthetic (example, synthetic gel zeolites)

- B. Organic
  - 1. Natural origin
    - a. Unmodified (examples, peat, lignite)
    - b. Modified (example, sulfonated coal)
  - 2. Synthetic (chemical constitution fairly well defined)
    - a. Tannin-formaldehyde resins
    - b. Phenol-formaldehyde resins

II. Anion-exchange Adsorbents

- A. Inorganic
  - 1. Natural origin (example, dolomite)
  - 2. Synthetic (example, heavy-metal silicates)
- B. Organic
  - 1. Natural origin
    - a. Unmodified (examples, horn, wool)
    - b. Modified (example, alkali-treated asphalt)
  - 2. Synthetic (example, amine-formaldehyde resin)

<u>Type Reactions</u>. The fundamental ion exchange reactions are few and simple(26). Cation exchange may be carried out according to the "salt cycle" in which one metallic or organic cation is replaced by another:

$$Ca^{++} + Na_2Z^* \underset{\text{Regeneration}}{\overset{\text{Reaction}}{\rightleftarrows}} 2\ Na^+ + CaZ$$

* Z represents Cation exchanger.

or according to the "hydrogen cycle" in which all metallic or organic cations in solution are replaced by hydrogen ions provided by an acid-regenerated cation exchanger:

$$2\ Na^+ + H_2Z \underset{\text{Regeneration}}{\overset{\text{Reaction}}{\rightleftharpoons}} 2\ H^+ + Na_2Z$$

The reactions(3) of the cation exchangers being true equilibria reactions, conform to the Law of Mass Action, and an increase in concentration of the products will effect a reversal of the equilibrium. Generally, an appreciable excess of regenerant is used, and a relatively high concentration is employed so that revivefication of the exchanger will be essentially complete.

Anion exchangers may be used to carry out true anion exchange reactions of the type:

$$SO_4^{--} + 2(\overset{*}{R_3}NH)Cl \underset{\text{Regeneration}}{\overset{\text{Reaction}}{\rightleftharpoons}} 2\ Cl^- + (R_3NH)_2SO_4$$

* R_3N represents free anion exchanger.

Anion exchange materials also effect acid removal:

$$CH_3COOH + R_3N \longrightarrow (R_3NH)OOCCH_3$$

in which case the anion exchanger is regenerated by treatment with a solution of an alkali:

$$(R_3NH)OOCCH_3 + NaOH \longrightarrow R_3N + CH_3COONa + H_2O$$

Schwartz, Edwards, and Boudreaux contend that in acid removal by ion exchange methods both true anion exchange, sometimes referred to as "salt formation", and whole molecule adsorption occur simultaneously(23).

Nachod and Wood(20) have found that reactions of anion exchange are 400 to 4000 times slower than cation exchange reactions.

<u>Ion Exchange Materials</u>. Walton(28) describes the various materials showing ion exchange. He states, "among the minerals in which ion exchange is most marked are alumino-silicates such as the zeolites,

montmorillonite and some other clay minerals, ultramarine, glauconite, and the chabazites. A smaller degree of ion exchange is found in the feldspars and kaolinite. All of these minerals contain alkali or alkaline earth metal ions, and it is these ions which will exchange with ions in solutions. The zeolite family consists of hydrated alumino-silicates that contain easily exchangeable ions such as sodium or potassium(24). The base-exchange substances may be represented by the general formula $Na_2O.Al_2O_3.nSiO_2.xH_2O$, where n represents 5 or more, and x represents varying amounts of water of hydration(24)(28)(30).

Among the natural organic compounds which have ion exchange properties are the humic acids and the proteins. The latter can exchange both cations and anions, whereas humic acids exchange only cations(28).

The anion exchange materials are not as numerous as base-exchange substances. The main anion exchange materials are: apatite, aromatic amine resins and aliphatic amine resins. Many others have been suggested and used with limited success(18): barium carbonate, iron oxide and aluminum oxide gels, zinc and other metallic oxides, basic dolomite, chlorinated coal, activated carbon, alkali-treated asphalt, horn, silk, wool and leather scrap.

<u>Applications of Ion Exchange</u>. Removal of undesirable ionic impurities from solutions is the most common process in which ion exchange is employed(26). Water softening processes using ion exchange materials have been given a great deal of attention in the literature(1)(3)(11)(18)(24)(27).

Ion exchange processes are frequently used for the recovery of valuable substances from solutions(26). For example, specific metals or groups of metals have been absorbed on cation exchangers for analytical purposes. Cation exchange has been used abroad for the recovery of copper from cuprammonium rayon waste liquors(26). Non-metallic cations are also recovered in this manner in two widely used analytical procedures: the thiochrome assay for Vitamin B_1(12) and the Folin method for ammonia nitrogen(26). The recovery of nicotine, quinine, and other alkaloids by cation exchange methods has been reported and is being further developed.

Valuable anions may be recovered by the use of anion exchangers. Matchett(15) developed such a process for the recovery of tartrates from grape wastes.

Englis and Fiess(7) state that elimination of the acid and mineral constituents from artichoke extract by ion exchangers produced a sirup of improved quality and flavor. Buck and Mottern(5) used an ion exchange stage in the treatment of apple sirup to remove malic acid and thus prevented the formation of calcium malate during the liming process producing a sweeter sirup.

In addition to true anion exchange, valuable acids may be recovered by adsorption on alkali-regenerated anion exchangers(2). In some cases acids may be present as impurities. Such is true in the case of formaldehyde made by the catalytic oxidation of methanol. The formaldehyde may contain as much as 0.05 to 0.08 percent formic acid. Amberlite IR-4B, an anion exchange synthetic resin, may be used to remove the acid without salt contamination(2). This reference stated: "In this particular example the acidic constituent removed was an impurity, but by the same process valuable acidic materials including amino acids, and certain pharmaceuticals may be recovered easily, efficiently, and economically by adsorption on Amberlite IR-4B."

D. ACETIC ACID RECOVERY

Vie(8) developed an apparatus for washing the vapors in the concentration of chestnut extract which permits recovery of 13.2 kilograms of acetic acid from 1,000 kilograms of 25° Be. extract. Recovery was effected either in the form $NaOAc.1.5H_2O$ or $Ca(OAc)_2$. Vie found that the cost of apparatus was large, corrosion was great, and the products were often colored. Depasse(6)(8), in a criticism of Vie's work said that the process could be made profitable if the apparatus were properly constructed and used. No details as to the nature of the equipment were given.

Othmer(22) proposed a method for the separation of water from acetic acid by azeotropic distillation but the process appears to be confined to liquors containing an initial concentration of at least 6 percent acetic acid due to economical reasons. Furthermore, Othmer indicated that in the process large quantities of water containing from 0.02 to 0.10 percent acetic acid were passed off as waste.

In 1941 Gonzales(8) attempted the removal of acetic acid from an acetic acid-water vapor mixture by absorption in 5 percent potassium hydroxide solution in a packed tower. His work was carried out using acetic acid solution concentrations of 0.1 to 5.0 percent. The degree of absorption ranged from 64.5 to 95.5 percent with the greatest absorption obtained when the acetic acid concentration was 0.1 percent or less. Gonzalez used a copper absorption tower and the product obtained was impure and highly colored, being contaminated with copper salts. Corrosion of the copper tower was very noticeable.

III. EXPERIMENTAL

A. Purpose of the Investigation

The purpose of this investigation is to recover acetic acid from the wastes of the tannin extract industry. Primary considerations will be given processes dealing with ion exchange materials.

B. Plan of Investigation

The general plan of procedure in this investigation is as follows:

1. Preliminary Investigation.
   a. Review of the Literature.
2. Design and Construction of Laboratory Apparatus for Recovery of Acetic Acid from Waste Liquor by Anion Exchange Resin.

Recovery of acetic acid from waste condensate liquor will be attempted by the use of a single ion exchange column. The ion exchange material to be utilized for this purpose will be De-Acidite, a synthetic anion exchange resin possessing high acid-binding capacity and long life.

The column will be of 25 mm. Pyrex glass tubing sufficiently long to contain 200 ml. of anion exchange resin with headspace available for 100% bed expansion. Below the bed within the column will be placed a supporting layer of crushed and sized porcelain. Glass wool will be used to prevent loss of solids in the column through the outlet tube at the bottom of the column. Inlet and outlet tubes to the column will be inserted through rubber stoppers sealing the top and bottom of the column. The apparatus will be constructed in such a manner that liquids will not come in contact with any metals.

In downflow operation, the column will be fed from open glass constant-head tanks above the column. All liquids to be passed through the column will be passed into the constant-head tanks from aspirator bottle reservoirs by gravity flow. Rates of flow through the column will be controlled by capillary tubes inserted in the outlet tube at the bottom of the column.

Backwash operations will utilize compressed air to force distilled water through the column from the bottom to an overflow exit at the top of the column.

3. Determination of Acid-Binding Capacity of Resin.

a. Total Acid-Binding Capacity

A batch operation will be carried out to expose 200 ml. of the ion exchange resin to a known volume of standard acetic acid solution. The reaction will be allowed to progress until maximum adsorption of the acid by the resin has taken place. During the course of the reaction intermittent samples of the acid solution will be withdrawn and tested to determine when equilibrium has been reached. The total acid-binding capacity of the resin will be determined by analyzing the final acid solution and taking into account the acid removed in the samples.

b. Acid-Binding Capacity at Breakthrough in Column Operation.

Dilute solutions of acetic acid will be used to partially exhaust the ion exchange resin in column operation. By means of colorimetric tests of the column effluent it is intended to determine the breakthrough point of unadsorbed acetic acid.

Varying rates of flow in succeeding experimental runs will be used to ascertain an optimum rate for maximum acid adsorption at breakthrough. Capillary tubes inserted in the effluent outlet at the base of the column will be used to control rates of flow of the effluent from the column.

4. Recovery of Acetic Acid from Waste Liquor.

It is well to recall that the waste liquor under consideration has, in addition to acetic acid, smaller amounts of other organic acids. In exposing the waste liquor to acid-binding resins, it is expected that the acids removed will be largely, but not entirely, acetic acid. Analysis of treated and untreated liquor will be total acidity expressed as acetic acid as recommended by Griffin(10). Henceforth, "acetic acid", so written, will denote the acid mixture.

a. Removal of "Acetic Acid" by Ion Exchange Resin.

The waste liquor will be passed downflow at the optimum rate as determined in 3b. above to determine breakthrough capacity. When the breakthrough point is reached, the influent to the column will be shut off.

b. Backwash.

To thoroughly reclassify the resin bed and to remove any foreign materials entering with the waste liquor the resin bed will be backwashed for 10 minutes following each exhaustion operation. During backwash, expansion of the bed will be maintained at 75 percent. Backwash water will be sent to waste.

5. Elution of "Acetic Acid" from De-Acidite.

The De-Acidite, partially saturated with "acetic acid" from the waste liquor, may be made to give up that "acetic acid" by displacement with a relatively stronger acid. Sulfuric acid in downflow operation will be used to accomplish elution in this case. Concentrations will be varied along with rates of flow to determine an optimum combination of concentration and rate for the elution. It is intended to terminate the elution process when sulfuric acid first appears in the effluent from the column. Barium chloride is to be used as a test for sulfates indicating breakthrough of sulfuric acid.

6. Concentration of "Acetic Acid".

Calcium Hydroxide is to be added to the "acetic acid" forming calcium acetate in water solution. The solution will be evaporated to dryness leaving calcium acetate. The calcium acetate will be treated with sulfuric acid to form acetic acid and calcium sulfate. Simple distillation will be used to obtain acetic acid as the final product.

7. Summation of Experimental Tests.

a. Total Capacity of Resin.

1. Conditions:

Variants	Non-Variants
None	Temperature: 20-30°C. Vol. of Resin: 200 ml. Vol. of Acid Soln.: 6.0 l. Conc. of Acid Soln.: 0.5% Time of Test: 4 hours

Ex. Test No. 1

b. Breakthrough Capacity of Resin.

1. Conditions:

Variants	Non-Variants
Rate of Flow of Acetic Acid Soln.	Temperature: 20-30°C. Conc. Acet. Acid: 0.2%

Ex. Test No.	Rate of Flow of Acetic Acid Solution, (gal./ft^2/min.)
2	1
3	3
4	5

c. Removal of "Acetic Acid" from Waste Liquor.

1. Conditions:

Variants	Non-Variants
None	Temperature: 20-30°C. Composition of Waste Liquor (approx. 0.02% Acetic Acid) Rate of Flow of Influent: Optimum as determined in 3b.

Ex. Run No. 5

d. Elution by Sulfuric Acid.

1. Conditions:

Variants	Non-Variants
Conc. H_2SO_4 Rate of Flow of H_2SO_4	Temperature: 20-30°C. Vol. Resin: 200 ml.

Ex. Test No.	Conc. H_2SO_4 %	Rate of Flow of H_2SO_4 (gal/ft^2/min)
6	4	3
7	4	4
8	4	5
9	10	3
10	10	4
11	10	5
12	15	3
13	15	4
14	15	5

e. **Concentration of "Acetic Acid".**

1. Formation of calcium acetate using lime.
2. Removal of water by evaporation.
3. Formation of acetic acid using H_2SO_4.
4. Separation of acetic acid from $CaSO_4$ by simple distillation.

Ex. Test No. 15

8. **Correlation of Data.**

C. Materials

The following materials were required for the investigation of recovery of acetic acid from wastes of tannin extract manufacture:

Raw Material

Waste Liquor. The waste liquor used was condensate from the second and third effects of a triple effect evaporator used by the Tanning Extract Division of the Mead Corporation, Lynchburg, Virginia, to concentrate tannin extracted from chestnut wood chips. The shipment of condensate varied in concentration between 0.02 and 0.05 percent total acidity expressed as acetic acid. The condensate used was clear and slightly yellow in color. Twenty gallons, received in five-gallon glass bottles, were used during the investigation.

Anion Exchange Resin

De-Acidite. The adsorbent used in this work was De-Acidite, obtained from the Permutit Company, New York, N.Y.. One pound of De-Acidite, Sample No. 26872, was used for adsorption tests.

Chemicals

Acid, Acetic, glacial, C.P., Lot No. 82,646: Manufactured by the J.T. Baker Chemical Company, Phillipsburg, New Jersey. Two pounds were used for adsorption tests.

Acid, Hydrochloric, C.P., Sp. Gr. 1.19: Manufactured by the J.T. Baker Chemical Co., Phillipsburg, New Jersey. Eighty-five ml. were used to prepare standard solution for adjusting phenolphthalein indicator solution.

Acid, Sulfuric, C.P., Sp. Gr. 1.84, Lot No. 3754/3: Manufactured by the J.T. Baker Chemical Co., Phillipsburg, New Jersey. One pound used for digestion of crushed porcelain to produce an inert De-Acidite bed support.

Alcohol, Ethyl, 95 percent: Obtained from the Stock Room of the Department of Chemical Engineering, Virginia Polytechnic Institute, Blacksburg, Virginia. Fifty milliliters were used for preparation of phenolphthalein indicator solution.

Hide Powder, American Standard, Lot No. 22: Manufactured by the Keystone Tanning and Glue Co., Ridgway, Pennsylvania. Thirty grams used for analysis of waste liquor for tannin.

Hydroxide, Sodium, C.P. Pellets, Lot No. 71,346. Manufactured by the J.T. Baker Chemical Co., Phillipsburg, New Jersey. Three pounds were used for analytical reagent and regenerant solutions.

Kaolin, Technical Grade, Pulverized: Obtained from the Stock Room of the Department of Chemical Engineering, Virginia Polytechnic Institute, Blacksburg, Virginia. Eight grams used as filtering medium in analysis of waste liquor for tannin.

Methyl Orange, C.P., Powder, Lot No. 52,946: Manufactured by the J.T. Baker Chemical Co., Phillipsburg, New Jersey. One gram was used for preparation of one percent indicator solution.

Phenolphthalein, C.P., Lot No. 42,246: Manufactured by the J.T. Baker Chemical Co., Phillipsburg, New Jersey. One gram was used for preparation of one percent indicator solution.

Phthalate, Potassium Acid, C.P.: Manufactured by the Coleman and Bell Co., Norwood, Ohio. Ten grams were used for standardizing sodium hydroxide solutions.

Sulfate, Chromium Potassium, Analytical Grade: Manufactured by the Mallinckrodt Chemical Works, New York. Sixteen grams were used in analysis of waste liquor for tannins.

Water, Distilled, Ph 5.5-7.0: Distilled by and obtained from the Department of Chemistry, Virginia Polytechnic Institute, Blacksburg, Virginia. Used for all analytical, regenerant, backwash, and rinse solutions.

D. Apparatus

Experimental tests made during the course of this investigation were carried out using apparatus constructed by the author in the laboratory. Glass was used to prevent contamination of reaction materials. Materials of construction were obtained from the Stock Rooms of the Virginia Polytechnic Institute Department of Chemical Engineering and Department of Chemistry.

Agitator, electric, Fultorn Labmotor, (Volt 115, Cycles 60 AC): Distributed by Fisher Scientific Co., Pittsburgh, Pennsylvania. Used to agitate adsorption reactants in batch operation.

Balance, analytical, chainomatic, dampened, Serial No. C-77: Manufactured by Seederer Kohlbusck, Inc., Jersey City, New Jersey. Used for weight determinations.

Balance, rough, triple-beam, Maximum Capacity 610 grams: Manufactured by the Ohaus Company, Newark, New Jersey. Used for weighing acetic acid and sodium hydroxide.

Bottles, Aspirator, 4-liter: Obtained from the Stock Room of the Department of Chemistry, Virginia Polytechnic Institute, Blacksburg, Virginia. Three used for liquid feed reservoirs to the column.

Bottle, 5-gallon: Obtained from the Stock Room of the Department of Chemistry, Virginia Polytechnic Institute, Blacksburg, Virginia. One used for pressure backwash bottle in rinsing and regrading De-Acidite bed in column.

Box, wood, 9"x 6"x 3": Constructed from standard cigar box drilled on the ends to contain two Nessler Tubes for colorimetric comparisons.

Capillary Tubes, to deliver 20 ml./min.: Diameter of bore 0.60 mm. Length 66.5 mm.; to deliver 60 ml./min.: Diameter of bore 0.80 mm. Length 49.0 mm.; to deliver 100 ml./min.: Diameter of bore 1.0 mm. Length 24 mm. Used to control flow through column.

Compressor, Nash-Hytor, Size MD-2 L, R.P.M. 3500, Test No. 2007: Manufactured by the Nash Engineering Co., South Norwalk, Connecticutt. Used to furnish air pressure for backwash operations and air-lift pumps.

Crusher, Jaw, Blake type: (6" corrugated jaws): Manufactured by the Universal Crusher Co., Cedar Rapids, Iowa. Used for crushing 3/8" porcelain grinding balls for De-Acidite bed support.

Flask, round bottom, 12-liter, Pyrex: Manufactured by the Corning Glass Co., Corning, New York. Used to contain adsorption reactants in batch operation.

Mortor, iron, 9.5" high, 10.5" top diameter, 9" base diameter: Obtained from the Stock Room of the Department of Chemical Engineering, Virginia Polytechnic Institute, Blacksburg, Virginia. Used to support reaction flasks.

Nessler Tube, 50 ml., "Double-Plane": Distributed by the Fisher Scientific Co., Pittsburgh, Pennsylvania. Two used for colorimetric analysis of effluents from column.

Nessler Tube Illuminator, constant intensity, box type, 5"x 10" white glass lens; Light Source: two 150-watt General Electric lamps: Constructed of wood. Used as a light source for Nessler tube colorimetric comparisons.

Oven, electric drying, Serial No. 180B, Maximum Temperature 180°C, (Volt 115 AC, Watts 400): Obtained from Phipps and Bird, Inc., Richmond, Virginia. Used for drying samples.

Pump, Air-lift, blown from 7 mm. soft glass tubing, (see Detail, Drawing No. 2, page 27.) Used to recycle overflow from constant-head tanks to main reservoirs.

Riddle, Combs Gyratory: Manufactured by the Great Western Manufacturing Co., Leavenworth, Kansas. Used to vibrate screens in sizing porcelain granules.

Screens, U.S. Standard; (8-inch): Manufactured by Precision Scientific Co., Chicago, Illinois. Nest of two, meshes 20 and 30. Used to size porcelain granules.

Stand, ring, 34" high: Welded construction of 1/2" mild steel rod and 1"x1"x1/8" angle-iron. Obtained from the Department of Chemical Engineering, Virginia Polytechnic Institute, Blacksburg, Virginia. Used to support flask and agitator assembly.

Thermometer, mercury, 0-360°C.: Manufactured by the Will Corporation, Rochester, New York. Used to indicate all temperatures.

Timer, electric, Precision, "Time-it", (Volts 110 Cycles 60 AC): Manufactured by Precision Scientific Company, Chicago, Illinois. Used for all measurements of time.

Miscellaneous Apparatus: Beakers, 1000 ml., and 250 ml., 3 of each required; bottles, 250 ml., screw tops, 2 required; buchner funnel, 6" x 6", 1 required; burette, 1000 ml., 1 required; burette, 50 ml., 2 required; Erlenmeyer flasks, 250 ml., 4 required; evaporating dishes, 100 ml., 4 required; graduate cylinder, 500 ml., 1 required; funnel, 2-1/2" x 6", 2 required, pipettes, 100 ml., 50 ml., and 25 ml., 1 of each required; volumetric flasks, 100 ml., 250 ml., 500 ml., and 1000 ml., 2 of each required; watch glasses, spatulas, tube clamps, and stirring rods.

E. Method of Procedure

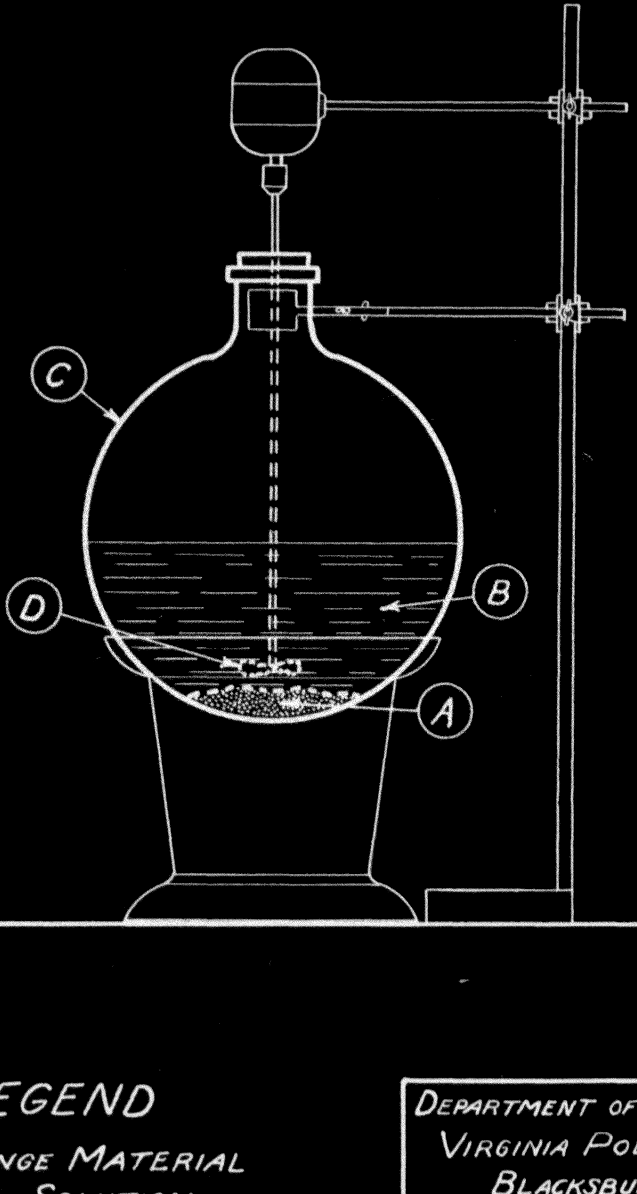
Construction of Ion Exchange Apparatus

Batch Apparatus. The ion exchange apparatus for batch operation was constructed as shown in Drawing No. 1, Page 26.

Column Apparatus. The apparatus for ion exchange using column operation was constructed as shown in Drawing No. 2, Page 27, using glass tubing, rubber tubing, and glass vessels supported by a welded 1/2" iron rod framework. A wood shelf 37" x 12" x 1" mounted on 1-1/4" x 1-1/4" x 1/4" welded angle-iron brackets was constructed to support the feed reservoirs to the column. Constant-head tanks of 35 mm. glass tubing were mounted to provide constant feed of influent solutions to the column. The column was fed through rubber tubes fitted with screw compression clamps to regulate flow rates.

For backwash operations a compression wash bottle was assembled with rubber tube conveying water to the base of the column. A separate replaceable outlet tube of glass was fitted with rubber stopper for use at the top of the column to carry off overflow water. A Nash-Hytor compressor was installed to provide air pressure for backwash operations and air-lift pumps.

Air-lift pumps were constructed from 7 mm. soft glass tubing and installed to pump overflow liquids from the constant-head tanks to the reservoirs feeding the constant-head tanks. The purpose of the air-lift pumps was to provide a continuous recycling of overflow liquid requiring minimum attention and less frequent refilling of the reservoirs during prolonged runs. It was found through trial and error using



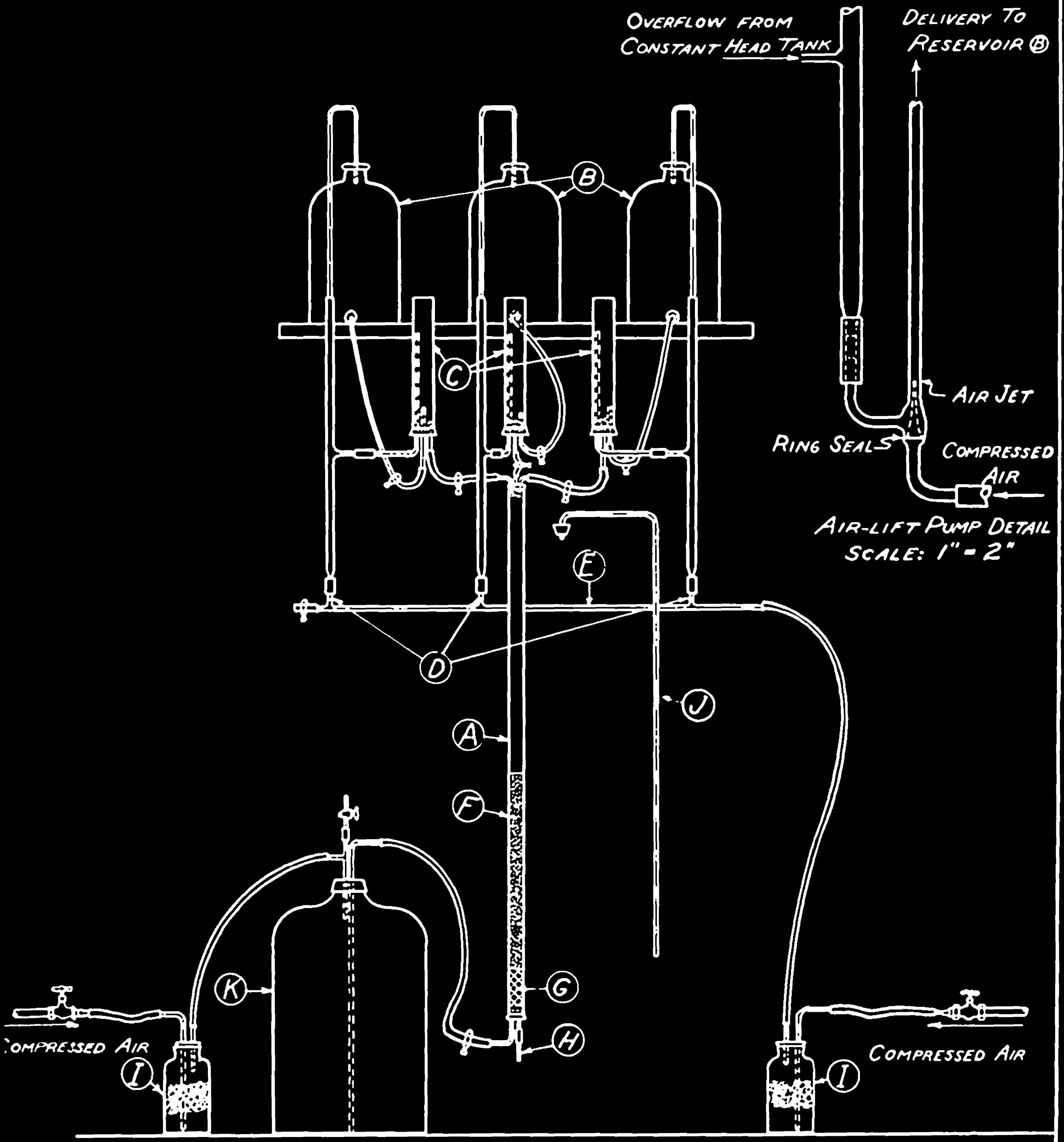
LEGEND

Ⓐ Ion Exchange Material
Ⓑ CH_3COOH Solution
Ⓒ Round Bottom Flask, 12 Liter
Ⓓ Agitator

Department of Chemical Engineering
Virginia Polytechnic Institute
Blacksburg, Virginia

ION EXCHANGE APPARATUS BATCH OPERATION

Scale: 1" = 6"	Case No.
Drawn By: F.E.T.	File No.
Checked By: F.C.V.	Drawing No. 1
Approved By: F.C.V.	Date: Mar. 3, 1947



(A) Ion Exchange Column, 25mm I.D., 41 in Long
(B) Aspirator Bottles, 4-Liter
(C) Constant Head Tanks, 1.5 in. I.D., 9.5 in. Long
(D) Air-lift Pump, Blown Glass (See Detail)
(E) Intake Air Manifold for Air-lift Pump
(F) Ion Exchange Material, 200 ml.
(G) Porcelain, Crushed and Sieved, -20 +30 Mesh
(H) Capillary Tube
(I) Air Filter, Glass Wool Maze Type
(J) Column Backwash Overflow Tube (Disconnected)
(K) Pressure Wash Bottle, 5-Gallon Cap.

Department of Chemical Engineering
Virginia Polytechnic Institute
Blacksburg, Virginia

ION EXCHANGE COLUMN & AUXILIARY EQUIPMENT

Scale: 1" = 8"	Case No.
Drawn By: F.L.T.	File No.
Checked By: T.C.U.	Drawing No. 2
Approved By: T.C.U.	Date: Feb. 18, 1947

5, 6, 7, and 8 mm. tubing that the 7 mm. size gave most satisfactory operation for pumping water at temperatures within 20-30° Centigrade. Excessive resistance to flow was noted in the 5 and 6 mm. tubing. In the 8 mm. tubing it was found that the cross-sectional area inside the tube was too large. This resulted in rupture of the meniscuses of the layers of water separated by air in the tube leading to the reservoir. The rupture produced a countercurrent stream of liquid returning to the pump along the interior wall of the same tube. Maximum hydrostatic head acting on the pump feed at the air-jet level was necessary for satisfactory operation. To attain this, 50 ml. burette tubes, from which stopcocks had been removed and a glass tee formed at the 25 ml. level, were utilized. The overflow from the constant-head tank was passed to the pump through the tee inlet to the burette. Maximum height of the overflow liquid was maintained in the burette with care taken not to exceed the overflow level of the constant-head tank concerned.

Air supplied to the air-lift pumps was passed through a glass wool maze filter contained in a 250 ml. sample bottle fitted with a rubber stopper secured in place by a bakelite threaded top. Before assembly, the bakelite top was drilled to accomodate the inlet and outlet tubes extending through the stopper into the bottle. The purpose of the filter was to prevent entrained moisture and rust particles from entering column influent solutions. Air activating the pumps was passed from the filter to a common manifold supply. The assembly was arranged so one or all three air-lift pumps could be operated at any time.

Preparation of Column

The column was prepared for operation by the following procedure:

The rubber stopper at the base of the column, with proper outlets, was tightly secured. Through the top of the column a wad of glass wool 1/2" thick was inserted and pressed into place against the bottom of the column. Granulated porcelain, previously sized to -20 +30 mesh, digested with boiling sulfuric acid, and rinsed thoroughly with distilled water, was poured into the column to a depth of 3 inches. The purpose of the porcelain was to provide a heavy inert support for the ion exchange material. With the effluent outlet closed, backwash water was forced into the column until the water level and porcelain level were the same. This point was marked on the outside of the column and became the zero point on a linear centimeter scale extending upward along the entire length of the column.

To determine the upper level of 200 ml. of ion exchange material in the column, 200 ml. of water at 26°C. was added to the contents of the column. This level was observed to be 41 cm. on the scale.

De-Acidite as received in Sample No. 26,872, in excess of 200 ml. was weighed and added through the top of the column. The De-Acidite was allowed to stand immersed in water in the column for 12 hours to permit volume expansion due to wetting. The column was backwashed at 75 percent bed expansion without loss of solids from the column and allowed to drain at maximum rate upon closure of backwash inlet. This backwashed and drained volume was observed to be 44.8 cm.

Regeneration of the De-Acidite bed was effected to insure the absence of swelling due to partial adsorption of acids. The bed was regenerated with 1,000 ml. of 1 percent sodium hydroxide in downflow operation at a rate of approximately 13.5 ml./min.

Rinsing was accomplished using downflow operation first at a slow rinse rate of 4.5 ml./min. until 300 ml. of effluent were collected. The slow rinse was followed by a fast rinse of approximately 60 ml./min. until 2,700 ml. of rinse water had passed through the bed. Rinse procedure in this case was as recommended by the Permutit Company, New York, N.Y., suppliers of the De-Acidite. It was observed that channeling in the bed during downflow rinse prevented complete removal of the excess NaOH. Subsequent rinse operations were made by backwash operations at 75 percent bed expansion. Rinsing under these conditions insured the absence of channels. Rinse was carried on for approximately 4 hours at which time the overflow rinse water was tested qualitatively for alkalinity. If NaOH were present the rinse would be continued until none was detected.

To adjust the De-Acidite bed volume to 200 ml., backwash was employed at sufficient rate to remove that portion of De-Acidite above the 41 cm. level in the column. This process was carried out for four hours with intermittent draining to ascertain the remaining De-Acidite bed volume in the column. Removal of the fines from the bed and classification of the bed was accomplished as adjustment was performed. The weight of the De-Acidite finally retained in the column was determined by multiplying the original weight of De-Acidite in the column by the fraction: final backwashed and drained (B & D) height/original backwashed and drained (B & D) height. All De-Acidite weights were converted to dry basis.

Capillary Tubes. Capillary tubes were used at the base of the column by insertion into a rubber connection. This means was used to control rate of flow of effluent from the column during downflow operations. Various rates were possible by the use of capillary tubes of various diameters of bore and lengths. The tubes used in the investigation were as shown in Table I:

Table I

Sizes of Capillary Tubes with Rates of Flow

Rate of Flow ml./min.	Diameter of Bore mm.	Length of Tube mm.
20	0.6	66.5
60	0.8	49.0
100	1.0	24.0

Selection of the proper capillary tube length was made by passing distilled water through the column containing 200 ml. of De-Acidite, porcelain granules and thin layer of glass wool. A constant level of water was maintained in the column at 50 cm. height. The effluent from the column was allowed to flow through the capillary tube and collected. Time required for a given volume of flow was observed and the rate calculated. In this manner the proper length and diameter of the capillary tube was found by successive trial and error attempts. The final size tubes were those which would give the correct volume of effluent over a period of at least five minutes.

Total Acid-Binding Capacity of De-Acidite

The total acid-binding capacity of De-Acidite was determined by means of a batch operation conducted in the apparatus shown in Drawing No. 1, Page 26. The total capacity was determined to establish a basis for comparing breakthrough capacities to be obtained later in column operations.

The procedure used In Run No. 1 was as follows: Six liters of 0.0980 Normal acetic acid were measured into the reaction flask. A moisture determination was made on the De-Acidite material to be used. A weighed quantity of De-Acidite equivalent to the weight of the dry De-Acidite contained in the column as described above, was placed in the reaction flask with the acid. Agitation was performed continuously. At the end of thirty minutes two fifty milliliter samples of the liquid were removed from the reaction vessel and analyzed by titration with sodium hydroxide, using one percent phenolphthalein indicator solution. Sampling was repeated at the end of the first hour and each hour thereafter for five hours. The temperature of the reaction materials was maintained at 20-30°C.

Acid-Binding Capacity of De-Acidite
at Breakthrough in Column Operation

Optimum Rate of Flow. To ascertain which of three rates of flow, 1, 3, and 5 gal./ft.^{2}/min., would produce the greatest acid-binding capacity at breakthrough, runs were made at each rate. The procedure followed in each run was: The aspirator bottle reservoir was filled with an acetic acid solution of approximately 0.2 percent concentration. The feed line from the reservoir to the constant-head tank was opened and the constant-head overflow allowed to enter the air-lift pump and returned to the reservoir. After insertion of the desired capillary rate control tube in the effluent exit from the column, the feed line from the constant-head tank to the top of the ion exchange column was opened. Simultaneously, the closure clamp on the effluent tube was removed. The rate of feed to the column was regulated to equal the rate of effluent leaving by careful adjustment of the screw compression clamp controlling the feed to the column until the liquid level remained constant in the column at the 50 cm. level.

The effluent was collected in volumetric flasks and time of passage of each volume collected was noted. Sampling of the effluent for acid content was accomplished by withdrawing 50 ml. from each 150 ml. issuing from the column. Using methyl orange as an indicator, the sample was tested for acidity by colorimetric comparison against a blank containing an equal amount of methyl orange indicator. The tests were conducted in Nessler tubes mounted in a wood box excluding all light except that entering the tube ends and passing through the entire depth of sample. A Nessler tube illuminator of constant light intensity was utilized to aid in maintaining constant conditions for testing. The total acid-free effluent passing before acids were detected in the samples was used to calculate the acid-binding capacity of De-Acidite at breakthrough. The capacity was expressed as grains $CaCO_3$/cu. ft. of De-Acidite.

Removal of "Acetic Acid" from Waste Liquor

The procedure to remove the acids from waste liquor was identical to that described above for determining breakthrough capacity in column operation with the exceptions that waste liquor was used instead of a dilute solution of acetic acid, and a single rate of flow was employed. The waste liquor used was a solution of equal volumes of 2nd and 3rd effect evaporator condensate received from the Mead Corporation, Lynchburg, Virginia. Analysis of the combined condensates was made to determine the normality as acetic acid.

Analysis of Waste Liquor for Tannin

Tannin analyses were made on the waste liquor used in this investigation by two methods. The first method followed was the Official Method(21) of the American Leather Chemists Association for the analysis of vegetable extracts containing tannin. The procedure followed was modified to the extent that special shakers and evaporating and drying equipment called for were not used. The second method of analysis was the Loewenthal-Proctor Method for Total Astringency(32).

F. Data and Results

Moisture Determination

To enable weight conversion of De-Acidite Sample No. 26,872 to the dry basis it was necessary to make a moisture determination of the wet resin. The following data and results were obtained:

Table II

Determination of Moisture in De-Acidite

Sample No. 26,872

Drying Conditions: Temperature, 95°C.; Time, 16 hours

De-Acidite Sample No.	Weight of Watch Glass gms.	Wgt. of Watch Glass & De-Acidite (Wet) gms.	Weight of Wet De-Acidite Sample gms.	Wgt. of De-Acidite and Watch Glass After Drying gms.	Moisture %
1	10.1140	12.8651	2.7511	11.2002	60.52
2	10.7892	13.5410	2.7518	11.8718	60.66
				Average Moisture:	60.59

The average moisture content (60.59%) was used for subsequent weight conversions to dry basis.

Total Acid-Binding Capacity of De-Acidite

An experiment was made to determine the total acid-binding capacity of De-Acidite by reaching equilibrium adsorption conditions in batch operation. The data and results obtained are outlined in the following table:

Table III

Total Acid-Binding Capacity of De-Acidite in Adsorbing Acetic Acid

Conditions: 200 ml. De-Acidite (35.15 gms. dry basis)
5,925 ml. acetic acid, 0.0980 N
Temperature: 26°C.
Duration of test: 5 hours

Time hrs.	Sample Withdrawn ml.	Conc. of Acetic Acid Solution N	Acetic Acid Adsorbed gms.	Acetic Acid Adsorbed milli-mols/ gm.	Adsorption as gr. $CaCO_3$/ ft.^{3}
0	75	0.0980	0	0	0
1/2	25	0.0687	10.43	4.93	19,100
1-5	200	0.0682	10.71	5.07	19,700

In Table III it will be noted that Times 1 through 5 hours have been combined. This was done for simplicity since maximum adsorption was reached at the end of 1 hour and remained constant over the period remaining. Fig. 1, Page 37, is a graphical representation of the adsorption observed in this experiment.

Acid-Binding Capacity of De-Acidite at Breakthrough in Column Operation

Optimum Rate of Flow. Experiments were conducted using approximate rates of flow through the column of 1, 3, and 5 gals./ft.^{2}/min. measured by observing the equivalents in ml./min. In the 25 mm. (inside

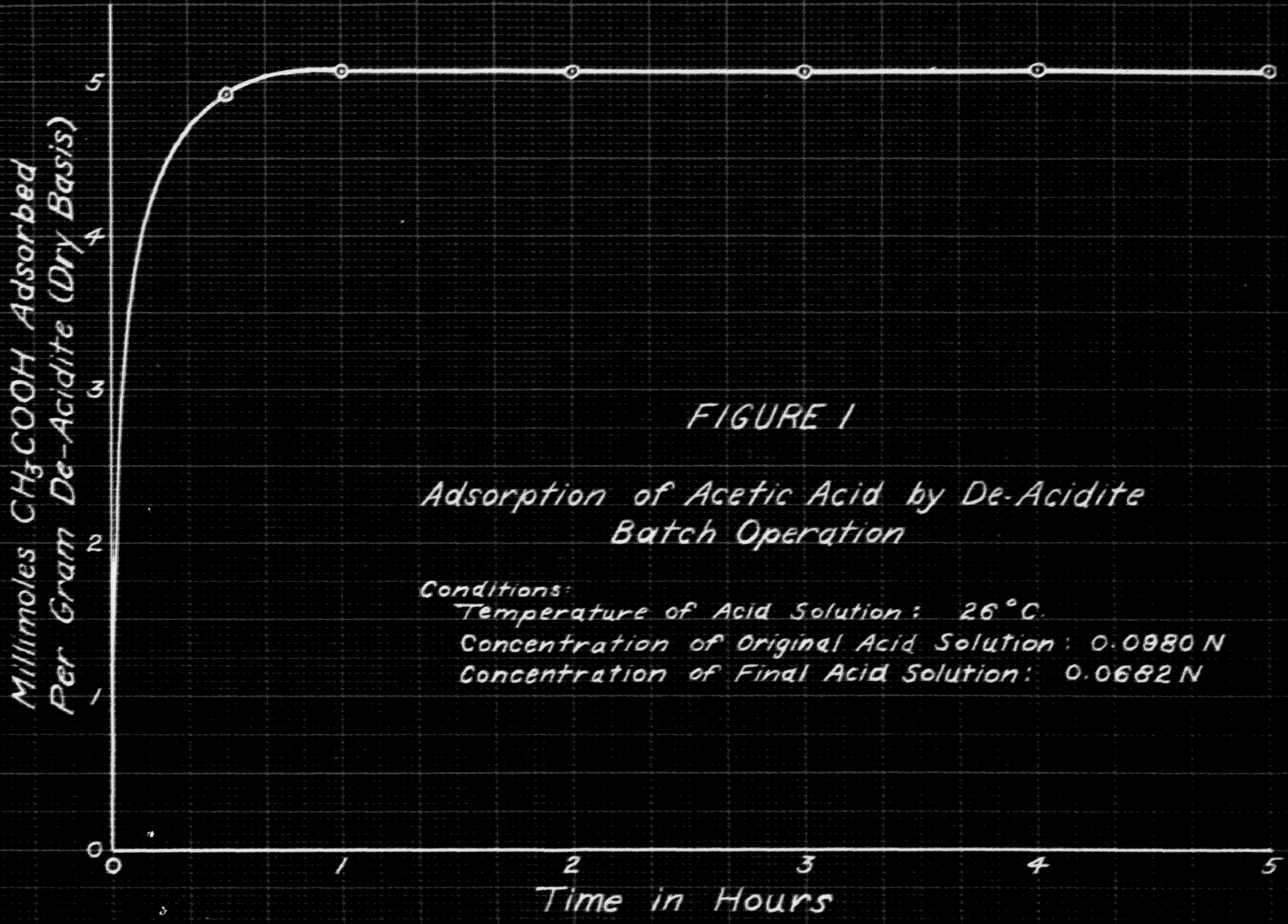


FIGURE I

Adsorption of Acetic Acid by De-Acidite
Batch Operation

Conditions:
Temperature of Acid Solution: 26 °C.
Concentration of Original Acid Solution: 0.0880 N
Concentration of Final Acid Solution: 0.0682 N

diameter) column, 20, 60, and 100 ml./min. were equivalent to 1, 3, and 5 gals./ft.^{2}/min. respectively.

The acid-binding capacities obtained at various rates of flow through the column are compiled in Table IV:

Table IV

Breakthrough Capacity of De-Acidite at Various Rates of Flow

Conditions: Temperature of Influent: 20-30°C.
Concentration of Influent: 0.0319 N
Volume of De-Acidite: 200 ml.
Regeneration: 850 ml. 1% NaOH
Rinse: Backwash at 75% expansion until free of alkalinity

Runs No.	Capillary Tube Used ml./min	Average Rate of Flow ml./min.	Breakthrough Capacity as gr.$CaCO_3$/ft.^{3}	Fraction of Total Capacity %
2e	20	20.4	12,300	62.5
3a, 3b	60	51.9	10,650	54.1
4, 4a	100	70.3	11,080	56.2

Rates of flow and capacities shown above are averages in those cases where two or more runs were made. The rate of flow for any given run varied during the course of the run and the average rate of flow was used.

In each run made to determine the optimum rate of flow it was observed that the rate of flow through the column decreased as time increased during the run due to packing of the ion exchange material in the bed. This phenomena is indicated in Table IV above when the average rate of flow is compared to the rate of flow for which the controlling capillary tube was calibrated. A graphical representation of the change of rate of flow appears in Fig. 2, 3, and 4 for flow controlled by 20, 60, and 100 ml./min. capillary tubes respectively.

Effect of Method of Rinse on Capacity. Two runs were made in the column apparatus after rinsing downflow with slow and fast rinse rates as explained in Method of Procedure, Page 30. Although rinse effluents obtained were free of alkalinity when tested with phenolphthalein, higher capacities resulted in the subsequent adsorption tests. Data and results obtained in runs following rinse by downflow are as follows in Table V:

Table V

Indicated Breakthrough Capacity

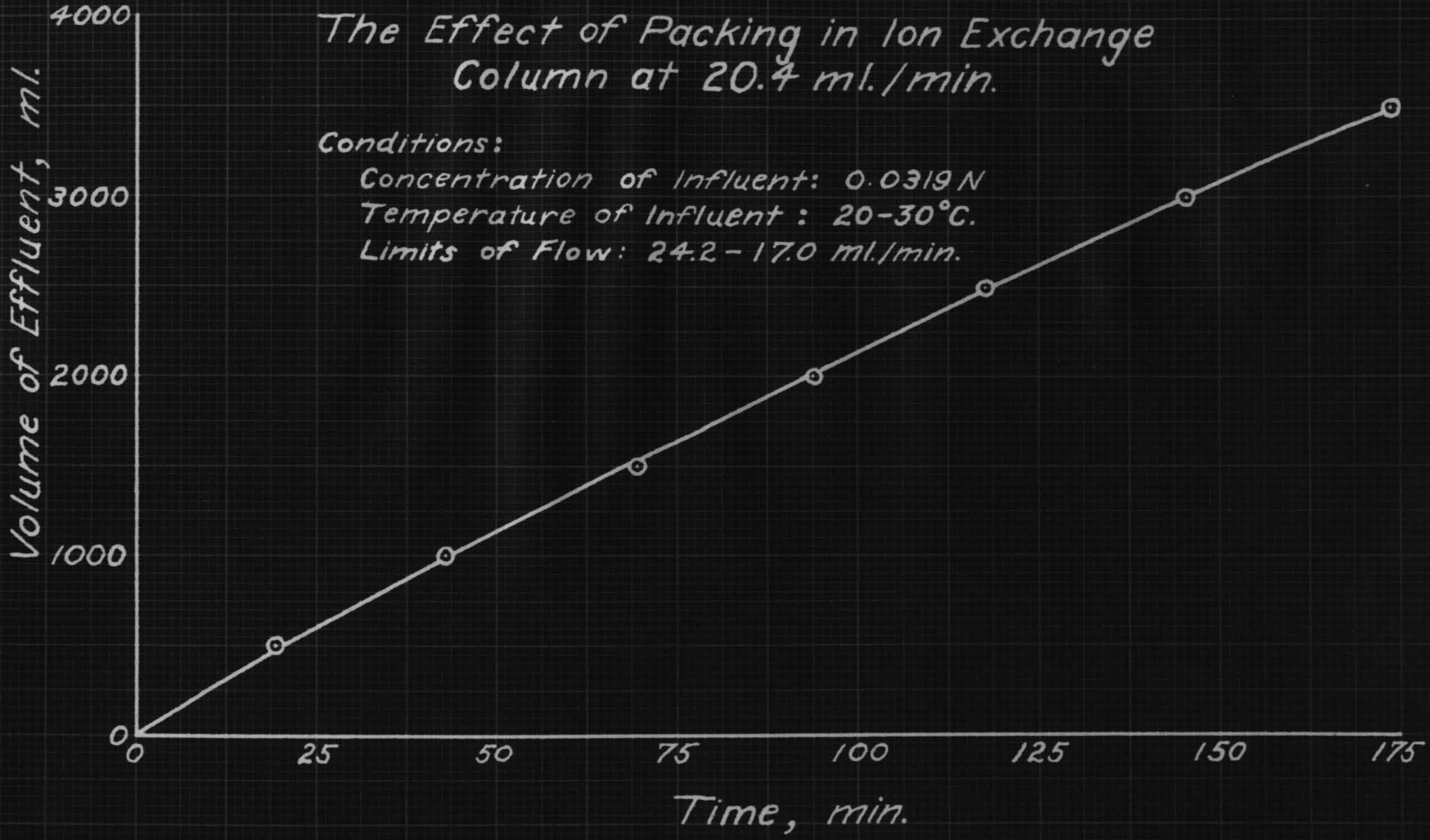
With Downflow Rinse

Conditions: Influent Concentrations: 0.0334 N
Temperature: 20-30°C
Volume of De-Acidite: 200 ml.
Rinse: Downflow until effluent free of alkalinity

Run	Preparatory Rinse				Influent Rate of Flow	Acid-Free Effluent	Indicated Breakthrough Capacity
	Slow		Fast				
	Vol.	Rate	Vol.	Rate			
No.	ml.	ml./min.	ml.	ml./min.	ml./min.	ml.	gr.$CaCO_3$/ft.^{3}
2a	315	6.8	3900	57.0	17.1	3,790	13,980
2b	300	4.5	2500	56.5	10.1	4,225	15,560

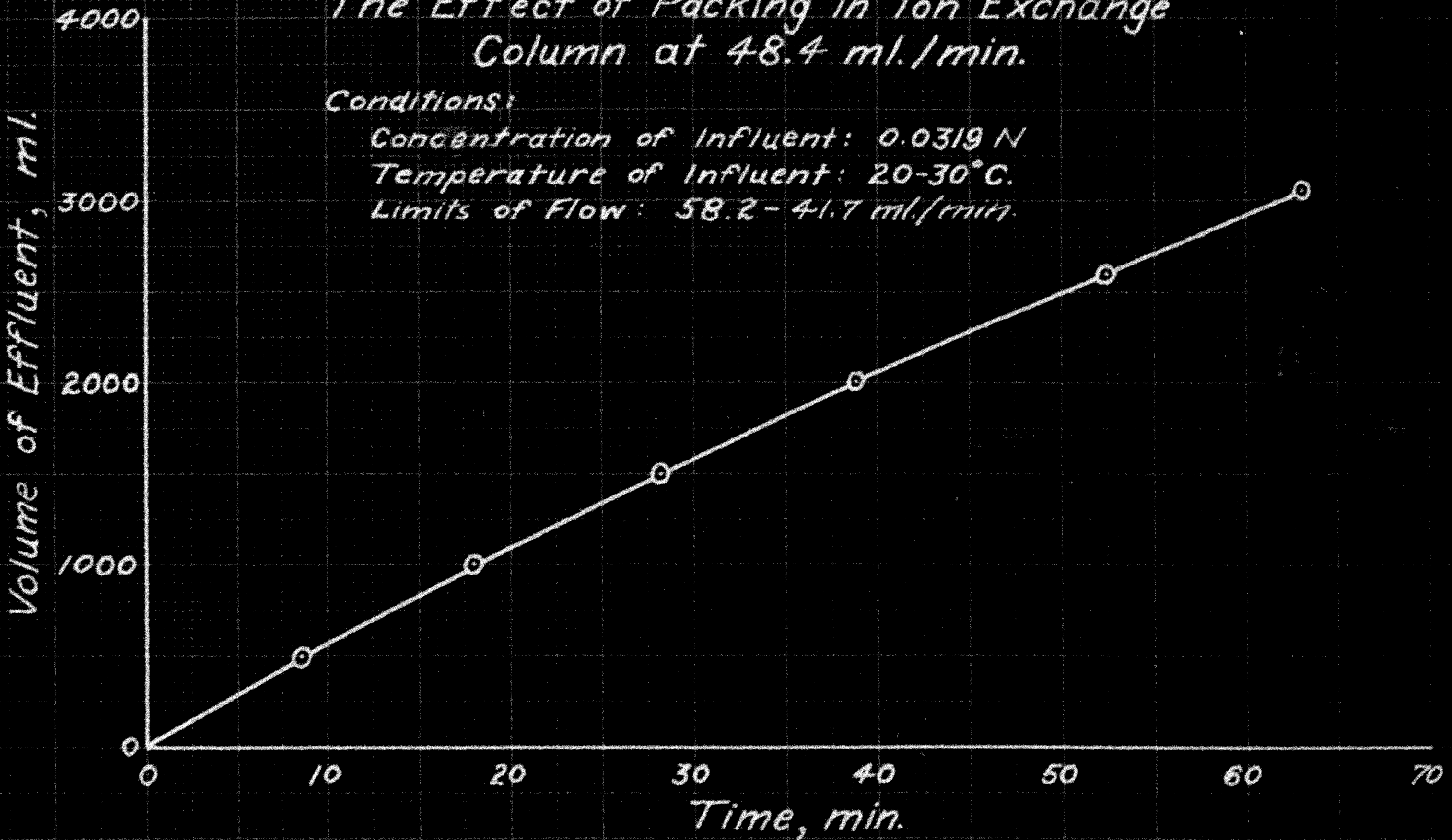
FIGURE 2

The Effect of Packing in Ion Exchange Column at 20.4 ml./min.



Conditions:
Concentration of Influent: 0.0319 N
Temperature of Influent: 20-30°C.
Limits of Flow: 24.2 - 17.0 ml./min.

FIGURE 3



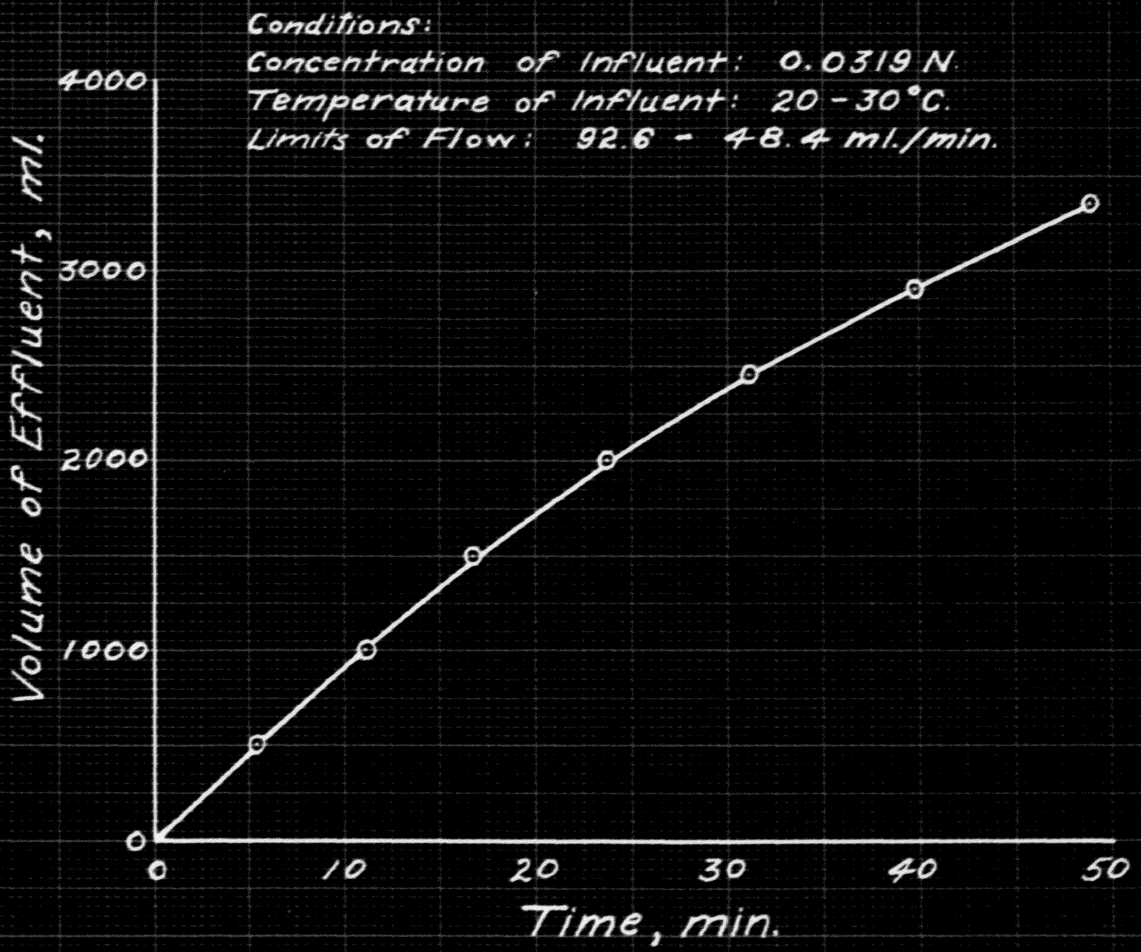
The Effect of Packing in Ion Exchange Column at 48.4 ml./min.

Conditions:

Concentration of Influent: 0.0319 N
Temperature of Influent: 20-30°C.
Limits of Flow: 58.2 - 41.7 ml./min.

FIGURE 4

The Effect of Packing in Ion Exchange Column at 69.9 ml./min.



Conditions:
Concentration of Influent: 0.0319 N.
Temperature of Influent: 20 - 30°C.
Limits of Flow: 92.6 - 48.4 ml./min.

Removal of "Acetic Acid" from Waste Liquor

A run was made to ascertain what acid-binding capacity De-Acidite would have at breakthrough when waste liquor was used as the column influent instead of a dilute solution of acetic acid. The waste liquor used for the test was a solution of equal volumes of condensate from the 2nd and 3rd effects of the triple effect evaporator employed by the Mead Corporation, Lynchburg, Virginia. By standardization of the mixed condensates against sodium hydroxide it was found that the acidity as acetic acid was 0.0065 N.

The data and results observed are as follows:

Table VI

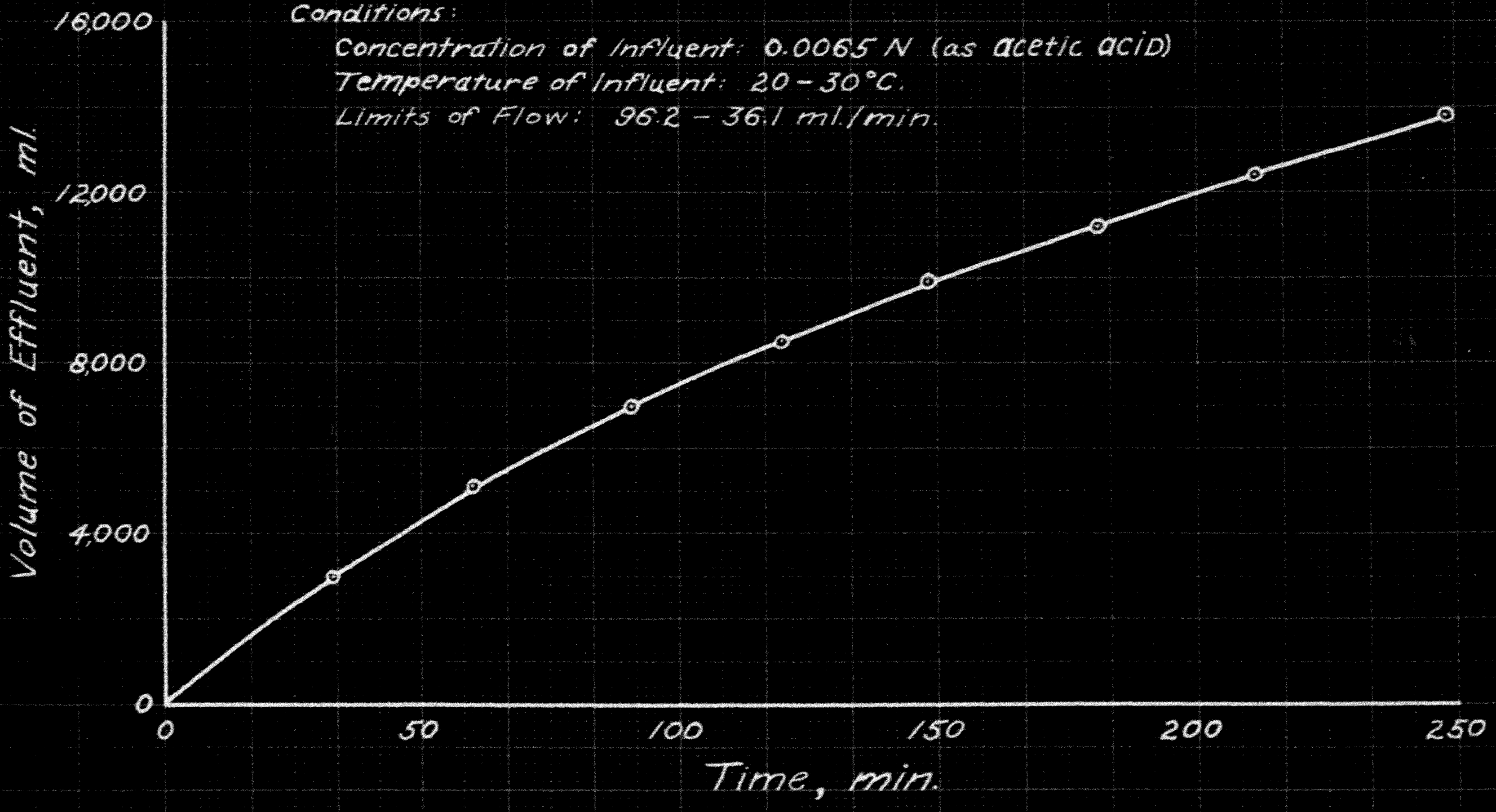
Breakthrough Capacity of De-Acidite in Adsorption of "Acetic Acid" from Waste Liquor

Conditions: Temperature of Influent: 26°C
Concentration of Influent: 0.0065 N
Regeneration: 940 ml. 1% NaOH
Rinse: Backwash at 75% of expansion until free of alkalinity

Run No.	Total Acid-Free Effluent ml.	Total Time min.	Average Rate of Flow ml./min.	Total Acid Removed or Acetic gms.	Breakthrough Capacity as $gr. CaCO_3/ft^3$	Fraction of Total Capacity %
5	13.800	248.3	55.6	5.39	9,900	50.3

FIGURE 5

The Effect of Packing in Ion Exchange Column
During Exposure to Waste Liquor at 55.6 ml./min.



Conditions:
Concentration of Influent: 0.0065 N (as acetic acid)
Temperature of Influent: 20 - 30 °C.
Limits of Flow: 96.2 - 36.1 ml./min.

Observations:

1. The clear amber colored De-Acidite turned dark brown or black as the waste liquor permeated the bed.

2. During backwash, for reclassifying the bed, following Run No. 5 it was observed that more fines existed than had previously been present after runs using pure acetic acid. No quantitative measurements were obtained however.

3. Backwash and drained height of the De-Acidite bed was 61 cm.

4. Regeneration of the De-Acidite after exposure to waste liquor failed to restore the original amber color. The regenerant effluent was clear but highly colored. The appearance was similar to strong tea.

Determination of Effect of Waste Liquor on Capacity of De-Acidite

It was believed that the darkened De-Acidite bed might have a different capacity than it had prior to exposure to waste liquor. Three runs were made using 0.0320 N acetic acid, 0.0065 N waste liquor, and 0.0320 N acetic acid in that order as column influents. By this procedure it was hoped to learn the effect of successive exposures of the ion exchange resin to waste liquor as compared to previous results obtained using dilute acetic acid solutions. The data and results obtained are compiled as follows:

Table VII

The Effect of Alternate Exposures of Waste Liquor and Acetic Acid on Breakthrough Capacity of De-Acidite

Conditions:	Run No. 6	Run No. 7	Run No. 8
Temp. of Influent:	25°C	24.5°C	25.5°C
Conc. of Influent:	0.0320 N	0.0065 N	0.0320 N
Vol. of De-Acidite:	200 ml.	200 ml.	200 ml.
Regenerant Vol.	880 ml.	870 ml.	865 ml.
Rate of Regenerant:	12.7 ml./min.	13.9 ml./min.	13.0 ml./min.
Rinse (Backwash):	NaOH-free	NaOH-free	NaOH-free

Run No.	Average Rate of Flow ml./min.	Total Acid-Free Effluent ml.	Total Acid Removed as Acetic grams	Breakthrough Capacity as gr.$CaCO_3$/ft.^{3}	Fraction of Total Capacity %
6	76.6	2,650	5.09	9,340	47.4
7	76.5	9,100	3.55	6,515	33.0
8	88.0	2,240	4.37	8,010	40.7

The conditions compiled in Table VII were those affecting the run under which they are enumerated. The regeneration was, as always, effected with 1 percent NaOH. The regeneration conditions refer to the regeneration carried out preceding the run concerned. The rinse by backwash was at 75 percent bed expansion in all cases.

Renewal of De-Acidite in Column. After replacing the used De-Acidite in the column with an equal volume of new material from Sample No. 26,872, three runs were made. The purpose was to determine if the breakthrough capacity of the new material would exhibit the same decrease upon exposure to waste liquor as had previously been the case. In using new De-Acidite the possibility that De-Acidite had undergone capacity reduction due to repeated cycles of exhaustion and regeneration would be eliminated.

The data and results obtained in this phase of the investigation are as follows:

Table VIII

The Effect of Waste Liquor on Acid-Binding Capacity of Fresh De-Acidite

Conditions:	Run No. 9	Run No. 10	Run No. 11
Temp. of Influent:	26°C	26°C	27°C
Conc. of Influent:	0.0055 N	0.0055 N	0.0058 N
Vol. of De-Acidite:	200 ml.	200 ml.	200 ml.
Regenerant Vol.:	850 ml.	865 ml.	850 ml.
Rate of Regenerant:	13.3 ml./min.	13.6 ml./min.	13.4 ml./min.
Rinse (Backwash):	NaOH-free	NaOH-free	NaOH-free

Run No.	Average Rate of Flow ml./min.	Total Acid-Free Effluent ml.	Total Acid Removed as Acetic grams	Breakthrough Capacity as gr.$CaCO_3$/ft^3	Fraction of Total Capacity %
9	75.3	13,750	4.54	8,330	42.4
10	96.9	12,450	4.11	7,540	38.4
11	88.6	9,450	3.12	5,720	29.1

Observations:

1. The amber color of the new De-Acidite turned black with the passage of less than 1,000 ml. of waste liquor in Run No. 9. This condition remained throughout the period required for completion of Run No. 9 and the subsequent Runs No. 10, and 11.

2. The regenerant effluents of all runs were clear and slightly amber colored.

3. The De-Acidite bed level in Run No. 9 increased from 41 cm. to 57 cm. (B and D). Regeneration following Run No. 9 failed to reduce the level to the normal 41 cm. level, but instead the backwashed and rinsed bed level was observed to be 44 cm.. Runs No. 10 and 11 were made with the ion exchange material occupying column volume up to 44 cm.

4. Small flaky particles and fines were excessive in the backwash overflow following each run. No quantitative measurements were obtained to establish the extent of ion exchange material lost in the fines.

Analysis of Waste Liquor for Tannin

Analysis of waste liquor used in this investigation was made by two methods: (1) the Official Method(21) of the American Leather Chemists Association for the Analysis of Vegetable Extracts Containing Tannin, and (2) the Loewenthal-Proctor(32) Method. The results obtained using the Official Method of the American Leather Chemists Association were erratic and no tannin content could be calculated from the data obtained.

The results obtained by the Loewenthal-Proctor Method reporting total astringency as tannin are as follows:

Tannin in 0.0065 N Waste Liquor - - - - 0.00098%

Tannin in 0.0055 N Waste Liquor - - - - 0.00196%

IV. DISCUSSION

A. Discussion of Results

Total Acid-Binding Capacity of De-Acidite. Determination of the total acid-binding capacity of De-Acidite was a basic prerequisite for calculating the fraction of the total capacity attained in succeeding runs made in column operation.

Since column operations were to be performed within the range of temperatures between 20-30°C., it was not necessary to maintain closer control of temperature in the batch operation to determine total capacity. However, temperature readings were taken at the beginning of the reaction and each hour thereafter; the temperature of the acetic acid solution remained at 26°C. throughout the experiment.

While the duration of the test was five hours, it was not known beforehand what the exact time would be before equilibrium conditions would exist. In any case the experiment was to be continued until maximum adsorption was attained. By observation of the adsorption curve, Fig. 1, Page 37, it is seen that maximum adsorption was reached within the first hour of contact between De-Acidite and the acetic acid solution. During the course of the experiment samples were taken at times: 0, 1/2, 1, 2, 3, 4, 5 hours. It would have been more satisfactory from the viewpoint of obtaining more points of data from which to plot a more accurate adsorption curve to have taken samples at 5-minute intervals during the first hour of the test when the quantity of acetic acid being adsorbed was changing rapidly. From the curve obtained it is estimated that 75 percent of all adsorption occurred in the first 5 minutes of reaction.

The total capacity found by this test was within the limits of the rated capacity of De-Acidite as stated by Sussman and Mindler(26), "12,000 to 25,000 grains per cubic foot (expressed as $CaCO_3$) depending on such factors as type of anion present, concentration, regenerant dosage, etc." No similar study has been located to which the results of this test can be more closely compared.

Acid-Binding Capacity of De-Acidite at Breakthrough in Column Operation

Apparatus. The apparatus used in this investigation was found very satisfactory from the standpoint of permitting duplication of conditions for successive runs. Ease of operation was of paramount importance since the method of sampling used required constant attention within itself. There was no difficulty encountered in maintaining constant feed to the column. Slight regulations in the rate of feed to the column were necessary to maintain a constant level of liquid within the column at the 50 cm. level. This was due to packing of the solids in the column with subsequent reductions in the rate of flow of liquids through the bed. Various degrees of channeling through the bed in the column also affected rates of flow and made necessary corresponding adjustments in the rate of feed to the column. No quantitative data was obtained on channeling effects except as it pertained to downflow rinse operations.

The capillary tubes used for controlling the rate of flow of effluent leaving the column have already been described along with the method of calibration. However, in calibrating the capillary tubes distilled water was used as the fluid medium and when the tubes were employed in the apparatus solutions of acetic acid or waste liquor were the fluids being controlled. It is not believed that any error was incurred in this procedure since the concentrations of both the acetic acid solutions and waste liquor were so dilute that the viscosity difference was negligible. On the other hand it is quite possible that the degree of packing in the column at the time of calibration was not the same as that packing developed during the course of prolonged runs.

Optimum Rate of Flow. In the technical pamphlet "Suggestions for Experimental Use of Ion Exchangers"(31), distributed by the Permutit Company, New York, N.Y., it is recommended that the downflow rate for exhausting De-Acidite in column operation be 50 ml./min. Since the pamphlet deals primarily with water softening it was not known whether the rate of 50 ml./min. would produce the maximum capacity at breakthrough when treating liquids containing acetic acid. Therefore, it was decided to use rates of 20, 60, and 100 ml./min. in an effort to determine an optimum rate of flow. The range of rates selected were those equivalent to the range commonly employed in filtering on an industrial scale. The concentration of acetic acid influents in these tests was 0.2 percent. While this concentration was greater than the concentration of acids in the waste liquor it was assumed that the optimum rate as determined would also be optimum for treating the waste liquor. The results of these experiments compiled in Table IV, Page 38, indicated that within the range of flow rates tested no material difference existed in the breakthrough capacity.

It was observed in the tests made for optimum rate of flow that the average rates of flow for any given run were generally less than the rate of flow for which the controlling capillary tube was calibrated. Run No. 2c had an average rate of flow of 20.4 ml./min when the 20 ml./min capillary tube was used to control the rate of flow. Fig. 2, Page 40, is a plot of the flow during the run and indicates the usual decrease in rate of flow with progression of time. The cause for the average rate of flow exceeding the calibrated rate of flow in Run No. 2c is attributed to fluctuations in the level of liquid in the ion exchange column and failure of the author to maintain the level constant at 50 cm.. In Runs No. 3a and 3b the average rate of flow was 51.9 ml./min. and the 60 ml./min capillary tube was employed. Fig. 3, Page 41, shows the decrease in the rate of flow with the passage of time of downflow operation in Run No. 3b. Similarly in Runs No. 4 and 4a the average rate of flow was 70.3 ml./min. when the 100 ml./min. capillary tube was used. Fig. 4, Page 42, is a graphical representation of the liquid flow in Run No. 4. Under the conditions used it can be seen that the deviation between averages of actual rates of flow and calibrated rates of flow of the capillary tubes increased as the magnitude of rate of flow increased. Such a condition is to be expected since packing within the column is more prevalent at the higher rates of flow.

The breakthrough capacities obtained in the tests for optimum rate of flow ranged from 54.1 to 62.5 percent of total capacity. The latter, 62.5 percent, was obtained at an average rate of 20.4 ml./min., the slowest rate tested. It was expected that this would be the case since the greatest time of contact for adsorption was obtained at the least rate of flow. The gain in adsorption capacity at the low rate would be offset by the necessity of a greater volume of De-Acidite per ion exchange unit or more adsorption units in treating a given volume of influent per unit of time as compared to treatment at the highest rate. For further experimental work in this investigation it was decided, for the economy of time, to use the maximum rate of flow employing the 100 ml./min. capillary tube.

Effect of Method of Rinse on Capacity. The Permutit Company(31) suggested that the rinse following regeneration of De-Acidite be accomplished using downflow operation with first a slow rate rinse of 4.5 ml./min. until the quantity of rinse water through the column reaches 300 ml.. This is followed by a fast rate rinse of 50 ml./min. until effluent alkalinity drops below a predetermined value. In this investigation it was found that 2700 ml. of fast rinse water were sufficient to indicate total removal of the excess regenerant from the De-Acidite bed. However, in rinsing by this method after the regeneration conducted following Run No. 2b, the liquid level in the column was accidentally allowed to drop below the top level of De-Acidite. As a result air entered the ion exchange bed and adhered to the De-Acidite particles. It was decided to correct the condition by backwashing for 10 minutes to dislodge the air. The author assumed that the backwash at this point would not materially affect the condition of the bed since the rinse by downflow had been completed. When the backwash overflow was tested for alkalinity with phenolphthalein it was observed that a deep pink coloration of the sample resulted. This indicated the presence of regenerant in the ion exchange bed even after downflow rinse effluent tests indicated total rinsing. Apparently total removal of the sodium hydroxide regenerant was not being accomplished during downflow rinse due to channeling within the bed.

Two runs, No. 2a and No. 2b, were made after the De-Acidite bed was conditioned by only downflow rinse. The results of these runs are shown in Table V, Page 39. The breakthrough capacities of 13,980 and 15,560 grains $CaCO_3/ft.^3$ obtained in Runs No. 2a and 2b respectively are considerably greater than the capacity obtained in Run No. 2c, amounting to 12,300 grains $CaCO_3/ft.^3$, after totally rinsing by backwash operation at 75 percent bed expansion. The high breakthrough capacities indicated in Runs No. 2a and 2b confirm the presence of unrinsed sodium hydroxide in the ion exchange bed. The effect of downflow rinsing, resulting in a bed only partially free of sodium hydroxide, is the neutralization of some acetic acid entering the bed instead of adsorption of that acid by the De-Acidite. The indicated breakthrough capacity under these conditions is not the true breakthrough capacity but is high by an amount equal to the amount of acid neutralized.

It was desired that the ion exchange bed be in the same condition for each run, or as nearly so as possible. Backwash rinsing was adopted throughout the remainder of the investigation.

<u>Removal of "Acetic Acid" from Waste Liquor</u>. It was desired to know the relationship between breakthrough capacity of De-Acidite using acetic acid solutions as influents and the breakthrough capacity using a waste liquor influent. Run No. 5 was conducted under the same conditions used in Runs No. 4 and 4a with the exception that waste liquor was used instead of acetic acid to obtain this comparison. It was found that the breakthrough capacity obtained using waste liquor was 9,900 grains

$CaCO_3/ft^3$ or 50.3 percent of the total capacity. In Runs No. 4 and 4a the average breakthrough capacity was 11,080 grains $CaCO_3/ft^3$ or 56.2 percent of total capacity when 0.2 percent acetic acid was used as influent. The waste liquor produced in this case a breakthrough capacity 5.9 percent below that experienced using acetic acid solutions.

The effects of waste liquor on the physical appearance of De-Acidite were pronounced. Immediately upon contact with the waste liquor the De-Acidite was subjected to a color change from its normal clear amber state to a dark coffee brown transmitting considerably less light through the bed. This color change could not be attributed to the acetic acid content of the waste liquor since previous exhaustions by acetic acid had not produced a noticeable change in the appearance of the De-Acidite. The waste liquor, being a condensate, could be considered virtually free of metals; a substance possibly present in the waste liquor would be tannin. Mindler(16) has stated that tannin-bearing liquors would have a marked deprecatory effect on the De-Acidite with rapid loss of capacity. Mindler also indicated that there existed an increase of fines after exposure to waste liquor.

A plot of the flow of waste liquor through the column in Run No. 5 is shown in Fig. 5, Page 44. The plot of volume of effluent versus time was seen to be of a parabolic nature. An empirical equation was found:

$$V + 2380 = 812.45\, t^{(0.5428)}$$

where:

V is the volume of effluent

t is time in minutes

Packing has been mentioned as a factor in decreasing the rate of flow of liquid through the ion exchange bed. In addition to normal packing, an inherent characteristic of De-Acidite is expansion upon adsorption of acids. As each individual particle expanded, the interstices between particles became smaller thus increasing resistance to flow. The effect of swelling was most obvious after exhaustion when the bed was backwashed to accomplish reclassification of the particles and remove foreign solids. For example, the backwashed and drained volume of De-Acidite in the column after Run No. 5 was 298 ml., an increase of 49 percent over the normal volume of 200 ml.

Regeneration of the De-Acidite bed following Run No. 5 was accomplished with 880 ml. of 1 percent sodium hydroxide solution. The regeneration failed to restore the clear amber color of the De-Acidite. The regenerant effluent was highly colored and reminded the author of strong tea. As regeneration proceeded the effluent became progressively less colored until at the end of regeneration a pale yellow effluent existed.

<u>The Effect of Alternate Exposures of Acetic Acid and Waste Liquor on De-Acidite</u>. Runs No. 6, 7, and 8 were concerned with finding what effect alternate exposures of waste liquor and acetic acid in separate successive runs would have on the breakthrough capacity of De-Acidite. The initial run in this series was made using 0.2 percent acetic acid. Run No. 7 had as an influent waste liquor and Run No. 8 repeated the use of 0.2 percent acetic acid. The data and results of these tests are compiled in Table VII, Page 46. Breakthrough capacities obtained in Runs No. 6 and 8 were 9340 and 8010 grains $CaCO_3/ft^3$ respectively compared to 11,080 grains

$CaCO_3/ft^3$ obtained averaging Runs No. 4 and 4a. Run No. 7 produced a breakthrough capacity of 6,515 grains $CaCO_3/ft^3$ as compared to 9,900 grains $CaCO_3/ft^3$ in Run No. 5. From these breakthrough capacities a marked decline in the efficiency of the De-Acidite is apparent; it may be postulated that further exposures to waste liquor would result in still lower ability of the ion exchange material to adsorb acids.

Renewal of De-Acidite in the Column. The same 200 ml. of De-Acidite have been used for the determination of breakthrough capacities for all runs in column operation through Run No. 8. In those runs using acetic acid solutions and waste liquor it was found that the waste liquor caused deterioration of the De-Acidite and a marked decrease in its effective acid-binding capacity. To preclude the possibility that the useful life of the De-Acidite had been reached due to 13 cycles of exhaustion and regeneration, and to find the effect of waste liquor alone on the resin, it was decided to make 3 runs with fresh De-Acidite in the column using waste liquor as the influent feed to be treated.

The data and results of Runs No. 9, 10, and 11 are compiled in Table VIII, Page 47. The fresh De-Acidite bed turned dark brown with the passage of 1,000 ml. of waste liquor in Run No. 9. The capacities of 8330, 7540, and 5720 grains $CaCO_3/ft^3$ were experienced in Runs No. 9, 10, and 11 respectively. These figures represent a decline of 13.3 percent of total capacity in three exposures of the resin to waste liquor.

An effect experienced in Run No. 9 not previously encountered was the failure of regeneration following the run to reduce the volume of the expanded bed to the normal 200 ml. The backwashed and drained volume of the bed after regeneration following Run No. 9 was 214 ml., and remained so in the same stage of the cycles in Runs No. 10 and 11. This condition could not be explained except by the possibility that the new batch of waste liquor used for these three runs may have had different composition than that previously used and therefore resulted in the permanently expanded condition of De-Acidite. Apparently, the expanded bed was more porous than the original De-Acidite bed since rates of flow in Runs No. 10 and 11 were 96.9 and 88.6 ml./min respectively as compared to 75.3 ml./min. in Run No. 9. The hydrostatic head within the column was maintained constant at 50 cm. for all three runs.

Analysis of Waste Liquor for Tannin. Analysis of the waste liquors used in this investigation for tannin content was made by two methods: the Official Method(21) of the American Leather Chemists Association, and the Loewenthal-Proctor(32) Method.

The results found by the Official Method of the American Leather Chemists Association were highly erratic making calculations of tannin content impossible. The cause of this was believed to be due to the fact that the tannin content of the waste liquor was less than the concentration range over which the method applies. In the procedure for the analysis it was stated that the sample should have not less than 0.375 grams of tannin per 100 ml. of sample nor more than 0.425 grams of tannin per 100 ml. of sample. Since the waste liquor is a condensate and not a leached extract the tannin content would necessarily be minute.

The results of the Loewenthal-Proctor Method are given on Page 48. The values computed are total astringency as tannin.

B. Recommendations

The following recommendations are made for future work on this subject:

1. Determination of Total Acid-Binding Capacity of De-Acidite. Samples of the acid solution used to totally exhaust the De-Acidite should be taken at intervals of 5 minutes during the first hour of the adsorption reaction. A device should be incorporated which would facilitate the withdrawal of samples without stopping the agitation within the system. The reaction vessel should be equipped with a thermometer for continuous indication of reactant temperatures. In this investigation 0.5 percent acetic acid solution was used to exhaust the De-Acidite. It is believed that a 0.2 percent acetic acid solution should be used with a corresponding reduction in the quantity of De-Acidite to insure an excess of acid at equilibrium conditions.

2. Breakthrough Capacity of De-Acidite in Column Operation.

a. Regeneration. In preparing the ion exchange bed between runs the regeneration should be accomplished with sodium carbonate to shorten the rinse period. Mindler(33) has suggested the use of aqueous ammonia for regeneration as an end toward the economy essential in waste recovery processes.

b. Rinse Method. It is recommended that rinse be by backwashing at 50 to 75 percent bed expansion. Backwash produces the necessary turbulence for the elimination of channels within the bed mass.

c. Optimum Rate of Flow. Tests were conducted in this study to determine the optimum rate of flow within the limits 1 to 5 gal./$ft.^2$/min. No substantial loss of capacity was observed at the maximum rate tested.

It is suggested that higher rates be tested to determine the maximum rate of flow possible before marked reduction of capacity occurs.

3. Removal of "Acetic Acid" from Waste Liquor.

a. Waste Liquor. The waste liquor used should be analyzed for the presence of organic substances other than tannin. An analysis for tannins should be developed suitable for accurately determining true tannin content when in extremely dilute solutions.

b. De-Acidite Fines. This investigation was carried out with no quantitative data obtained on the extent of formation of fines by exposure of the De-Acidite to waste liquor. Future work should include the determination of the amount of fines produced when De-Acidite is exposed to waste liquor and whether or not fines continue to form with repeated exposures.

c. Restoration of De-Acidite. Restoration of De-Acidite may be accomplished after its normal capacity has been blocked by contaminants in the waste liquor. Mindler(33) suggests treatment of the affected De-Acidite with 30 percent sulfuric acid at 60°C. for several hours followed by regeneration with soda ash. A valuable point brought out by Mindler was the fact that elution of "acetic acid" removed from the waste liquor by sulfuric acid would automatically overcome the decrease in capacity caused by the waste liquor.

d. Countercurrent Process. Mindler(33) suggested a process for economically recovering acetic acid from waste liquor which can best be stated in his own words: "The process I would suggest investigating includes taking up the acetic acid in a countercurrent manner by passing the solution through two beds of De-Acidite in series--the first bed being already partially exhausted and the second bed being freshly regenerated.

When the acetic acid breaks through the second bed, this bed will then receive the fresh acetic acid solution and an additional freshly regenerated De-Acidite unit would be cut into the line while the exhausted unit would be treated for recovery of the acetic acid. In order to reduce the chemical cost of the process, we believe it would be necessary to use a regenerant which could be recovered and reused. Such a regenerant would be aqueous ammonia. Thus, after the De-Acidite bed has been exhausted, 28% aqueous ammonia would be passed through the bed at a slow flow rate forming relatively concentrated ammonium acetate. The first portion of the effluent on introducing ammonium hydroxide would be merely displaced acetic acid. This would be diverted to the raw solution tank. Then, relatively concentrated, say 10-12% ammonium acetate would be recovered which would be diverted to a separate tank. The next portion of effluent would consist of a small amount of ammonium acetate contaminated with excess ammonium hydroxide which would be diverted to a separate tank for reuse in the next run prior to the introduction of 28% ammonium hydroxide. Finally, we would have diluted excess ammonium hydroxide solution which would be fortified with fresh ammonia.

The next step would be to decompose the ammonium acetate by suitable means, recovering the ammonia for reuse and leaving the acetic acid for further concentration by selective solvent action. I believe that organic acetate compounds are useful in this connection. The process of reusing ammonium compounds for regenerating base exchangers operating in the ammonium cycle was disclosed in U.S. Patent 2,397,575 "Method for Recovering Copper Value from Dilute Solutions of Copper Salts" issued to

Tiger and Goetz April 2, 1946. However, this process is distinct from regenerating anion exchangers."

V. CONCLUSIONS

From the results of this investigation the following conclusions were drawn:

1. When exhausted with 0.0980 N acetic acid at 26°C. the total capacity of De-Acidite is 19,700 grains $CaCO_3/ft^3$.

2. Maximum adsorption of 0.0980 N acetic acid by De-Acidite at 26°C. is obtained in batch operation in one hour.

3. In column operation at temperatures 20-30°C. using average rates of flow of 20.4, 51.9, and 70.3 ml./min. no material difference in breakthrough capacities occur when 0.0319 N acetic acid is used to exhaust 200 ml. of De-Acidite.

4. Downflow rinse to totally remove excess 1 percent NaOH regenerant from the De-Acidite bed is not effective under the following conditions due to channeling:

   a. Using distilled water; a slow rinse of 315 ml. at a rate of 6.8 ml./min followed by a fast rinse of 3900 ml. at a rate of 57 ml./min.

   b. Using distilled water; a slow rinse of 300 ml. at a rate of 4.5 ml./min followed by a fast rinse of 2500 ml. at a rate of 56.5 ml./min.

5. The adsorption of "acetic acid" from waste liquor in column operation by De-Acidite at 20-30°C. produces breakthrough capacities of 8330, 7540 and 5720 grains $CaCO_3$ per cu. ft. of De-Acidite when 0.0055 N,

0.0055 N, and 0.0058 N waste liquor is used at average rates of flow of 75.3, 96.9, and 88.6 ml./min. respectively.

6. The adsorption of acids from waste liquor is accompanied by:

   a. A degradation of the De-Acidite granules into flaky materials and fines.

   b. A color change of the De-Acidite from clear amber to a dark brown color.

7. Quantities of tannin in the waste liquor too minute to be determined by the Official Method of the American Leather Chemists Association for the Analysis of Vegetable Extracts Containing Tannin, and in the order of 0.00098 to 0.00196 percent total astringency as tannin when analyzed by the Loewenthal-Proctor Method, are sufficient to cause rapid depreciation of the De-Acidite and blocking of its effective acid-binding characteristics.

VI. SUMMARY

The tannin extract industry disposes of large volumes of condensate liquors evolved during concentration of weak leach liquors obtained by extraction of wood chips. The liquors are highly corrosive due to acetic acid contained therein along with lesser quantities of other organic substances common to woody materials. Recovery of the acetic acid would be desirable from two standpoints: (1) the value of the acetic acid, and (2) reuse of the acid-free condensate in the manufacturing process.

The purpose of this investigation was to recover acetic acid from the wastes of tannin extract manufacture. An ion exchange process was given primary consideration to accomplish the recovery by adsorption of the acetic acid from the waste liquor with subsequent elution of the acid from the ion exchange material by use of a stronger acid.

Tests were conducted using De-Acidite, a synthetic aliphatic amine anion exchange resin produced by the Permutit Company, New York, N.Y.. For all tests 200 ml. of the resin were used at temperatures within 20-30°C. A total acid-binding capacity of 19,700 grains $CaCO_3/ft.^3$ was found when De-Acidite was exposed to 0.5 percent acetic acid in batch operation.

Optimum rate of flow determinations in column operation within the range of 1 to 5 gal./$ft.^2$/min. were conducted. Variations of flow rates between these limits failed to produce substantial differences in breakthrough capacities.

To prepare the De-Acidite bed in the ion exchange column between runs regeneration was effected with 1 percent sodium hydroxide. Rinse was by downflow operation until data was obtained which indicated its unsuitability; thereafter backwash rinse was used and found more satisfactory.

The waste liquor used in the investigation was obtained from the 2nd and 3rd effects of a triple effect evaporator employed in the Mead Corporation Plant at Lynchburg, Virginia. Successive exposures of De-Acidite to the waste liquor resulted in sharp reduction of breakthrough capacity, discoloration of the De-Acidite, and deterioration of the resin with the formation of fines.

It was found that the extremely small quantities of tannin present in the waste liquor were the cause of the rapid depreciation of the De-Acidite.

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ADDENDA

31. Anon. Suggestions for Experimental Use of Ion Exchangers in the Process Industries. Pamphlet. The Permutit Company, New York, N.Y.

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