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# SUOMEN KEMISTISEURAN TIEDONANTOJA

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**Gösta Brunow**


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Sekreterare — Sihteeri
LARS-OLOF THODÉN Valhallagatan 3 Valhallankatu, Helsingfors 25 Helsinki, tel. 46 04 11 puh.

Kassör — Rahastonhoitaja
BJÖRN HOLM, Kaserng. 16 A 9 Kasarmink. Helsingfors 13 Helsinki, tel. 46 04 11, 63 96 70 puh.

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ANJA ANDERSEN, N. Hesperiag. 7 A P. Hesperiank. Helsingfors 26 Helsinki, tel. 49 08 78 puh.

Redaktör — Toimittaja
GÖSTA BRUNOW, Universitetets Kemiska Institut, S. Hesperiagatan 4 Helsingfors 10 Yliopiston Kemian Laitos, Et. Hesperiankatu 4 Helsinki 10 tel. 44 01 37 puh.


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# Preliminary Experiments with Preparation of Alkydes from Components Obtained from Spent Kraft Liquors by Heating with Alkali.

*By Terje Enkvist, Anja Andersen and Heikki Nupponen*

*Department of Chemistry, University of Helsinki—Helsingfors.*

## *Abstract*

A series of experiments were carried out in order to investigate to what extent substances obtained from spent liquors of the cellulose industry could be used at the manufacture of alkyd resins. I.a. the following conclusions seem to be justified (see p. 3):

Rosin acid mixture from tall oil gave alkyds which are only sparingly soluble in organic solvents and give high acid numbers. Use of fatty acids from tall oil made the alkyds soluble in styrene-methylmethacrylate 1:1 in many cases. In several cases such solutions could be polymerized by use of benzoyl peroxide catalyst, whereas irradiation gave poorer results. The polymerizates are often hard, cream colored and only slightly clouded, like some species of amber.

Succinic anhydride can be used instead of phthalic anhydride.

A combination of pentaerythritol and succinic anhydride, however, gives alkyds insoluble in the solvent mixture mentioned, even if fatty acid is used. Use of lactic acid in addition, however, gave a soluble alkyd.

Oxalic acid can be used as component in alkyds.

## *Investigation program*

By heating of kraft black liquor with added alkali considerable amount of oxalic, succinic, and homoprotocatechuic acids as well as pyrocatechol and some protocatechuic and lactic acid are formed (1). It would be of interest to know to what extent they might be used for different useful purposes. In the present paper preliminary experiments are reported, where some of these substances were used as components at the preparation of alkyd resins. Some of the resins obtained were further treated by dissolution in a mixture of styrene and methyl metacrylate and polymerization by gamma-radiation (cf 2) at the Institution of Radiochemistry of the University of Helsinki, or by slight heating with benzoyl peroxide as catalyst.

Together with the substances mentioned, several usual components of alkyds were used, mostly phthalic acid anhydride, glycerol, pentaerythritol and commercial fatty acid fraction from tall oil. In some cases experiments were made also with adipic, glutaric, isophthalic, vanillic, maleinic or oleic acid, with maleic anhydride, with benzyl lignin prepared from kraft black liquor (3), linseed oil or with sorbitol.



## *Experimental procedure*

In most of the experiments, the components used were mixed in stainless steel tubes, which were closed with silicon rubber stoppers. Glass distillation tubes inserted in the stoppers allowed water to distill off during heating. The tubes were heated in oil or metal baths. The temperature was measured.

After heating the reaction products were poured on watch glasses and their physical properties (solidity, brittleness, stickiness, hardness, transparence etc) were observed. Acid numbers as mg KOH/g were determined according to (4), and color determined according to (5). Of particular interest was the solubility in polymerizing solvents. In most cases a 1:1 solution of monostyrene and methyl metacrylate was used. In several cases where the alkyd samples could be dissolved in this solvent, the solution was polymerized by the use of:

a) addition of 1 % of benzoyl peroxide to a solution containing 20 % of alkyd and heating 20 h to 70°,
b) radiation 3,1 Mrad (31,8 kRad/h) of a solution containing 10 % of alkyd.

The properties of the solutions so treated were observed.

The main results of the experiments carried out are reported in the tables 1—6.

## *Discussion of results*

At the experiments reported in table 1 one of the main components was recrystallized rosin acid mixture from tall oil, so called "pinabietic acid" of Aschan (6, 7). This acid is well known as a reactive substance, easily oxidized by air and containing resin acids with conjugated double bonds. At $\gamma$-radiation of a sample it was swiftly changed to matter insoluble in petrol ether. A 10 % solution of fresh "pinabietic acid" dissolved in methyl metacrylate on $\gamma$-irradiation gave a hard, solid, tough and only slightly clouded and yellowish piece of resin.

For the use as a component of alkyds the slow esterification rate of rosin acid is a disadvantage. This can be seen in the exp. F2, F3, F5, F7 and F9—F11 in table 1. Also the exp. F1, F4, F6 and F8 in the same table show high acid numbers, probably caused by the use of free maleinic, adipic or oleinic acid. At the exp. 5a, 5b, 5c, 7d, 7e, 7f, 7h, and 7i, table 2, the cause of the high acid numbers also seem to be free acids, namely maleinic, succinic, protocatechuic or oxalic acid. In exp. 5, table 2, as well as in the cases XLII, XLVI—LIV, table 6, excess of lactic, isophthalic or fatty acids or of succinic and phtalic anhydrides compared with the amounts of alcohols used have perhaps caused the comparatively high acid numbers.

*Table 1.*

| Exp. No | Substances, g of each | Time hours | °C | Acid No | Consistence | Soluble in | Polymerate after radiation in S+MM[2]) |
|---|---|---|---|---|---|---|---|
| F1 | PA 2, M 6.0, A 3.6, E 6.6 | 10 | 200 | 81 | Clear liquid | MM | Precipitate |
| F2 | PA 3.6, M 5.8, R 4.6, G 6.0 | 20 | 200—250 | 97 | Hard solid | (MM)[1]) | Hard solid |
| F3 | PA 2.8, M 4.6, R 7.2, G 5.4 | 2 | 250 | <20 | Hard, brittle | — | — |
| F4 | M 2.4, G 5.6 | 10 | 250—300 | 87 | » » | AN[3]) | — |
| F5 | O 7.2, R 7.2, G 5.6 | 3 | 250—300 | 81 | L. yellow liq+prec. |  | — |
| F6 | PA 2.0, M 2.0, E 16.0 | — | — | — | Clear liq. | VA[3]) | Clouded |
| F7 | PA 2.8, O 4.4, R 6.8, G 6.0 | 15 | 200—210 | 65 | Cloud.liq. | — | — |
| F8 | PA 2.8, O 2.0, M 2.4, OL 6.8, G 6.0 | 10 | 200—210 | 68 | Viscous sticky liq. | — | — |
| F9 | PA 2.8, O 2.0, M 2.4, R 6.8, SO 6.0 | 12 | 200—250 | 135 | Hard, brittle brown solid | — | — |
| F10 | PA 2.6, M 2.2, PY 3.0, R 6.6, G 5.6 | 7 | 220—240 | 133 | L. brown sticky, visc. liq. | — | — |
| F11 | PA 2.8, M 2.2, PR 2.2, R 6.8, G 6.0 | 15 | 220—240 | 60 | Brittle, hard brown | — | — |

[1]) Only partly soluble.
[2]) Insoluble in St+MM and in vinyl acetate.
[3]) Insoluble in St.

— 4 —

*Table 2.*

| Exp. No | Substances, g of each | Time min. | C° | Acid No | Color Gardn. | Consistance | Sol.in S+MM | Polymerate peroxide[1]) | Polymerate radiation |
|---|---|---|---|---|---|---|---|---|---|
| 5 | PE 5, PA 5.4, F 5.5 | 20 | 240 | 100 | 10 | c. Hard, s. sticky | +++ | Hard, s. clouded | Viscous liquid |
| 5a | —»— + O 1.5, PE 1.25 | 20 | 240 | 103 | 5 | c. Hard, sticky | ++ | —»— | V-sc. liq., clouded |
| 5b | —»— + M 2, PE 1.3 | 20 | 240 | 114 | 7 | Hard, brittle | ++ | Hard, porous | —»— |
| 5c | —»— + S 2, PE 1.28 | 20 | 240 | 102 | 9 | c. hard, s. sticky, prec | (+) | —»—, prec. | Liquid |
| 5d | —»— + M 1, O 0.8, PE 1.3 | 20 | 240 |  | 5 | c. hard, s. sticky | ++ | Hard, porous | Visc. liquid |
| 5e | —»— + S 1, O 0.76, PE 1.28 | 20 | 240 |  | 9 | —»— | ++ | c. hard, s. clear | Visc. liq. clouded |
| 5g | —»— + PR 1.3, PE 0.32 | 20 | 240 |  | <18[2]) | —»— | + | Liq.+prec. | Liquid |
| 5h | —»— + PR 1.3, O 0.75, M 0.5, PE 1.27 | 20 | 240 |  | 12 | c. hard. c. sticky | + | —»— | » |
| 5i | —»— | 20 | 240 |  | 12 | —»— | + | —»— | » |
| 6 | PE 3.4, F 9.5, PA 3.7 | 360 | 250 | 21 | 6 | Viscous, sticky | ++ | Hard, cloudy | Soft, clouded |
| 7 | PE 2.0, PA 1.85, F 5.8 | 360 | 240 | 12 | 9 | —»— | +++ | —»— | —»— |
| 7a | —»— + O 1.3, PE 1.0 | 360 | 240 |  | 6 | Liquid, c. sticky | +++ | Liq., dark |  |
| 7b | —»— + M 1.7, PE 1.0 | 360 | 240 |  | 6 | Rubberlike, s. sticky |  |  |  |
| 7c | —»— + S 1.73, PE 1.0 | 360 | 240 |  | 10 | Liquid+prec. |  |  |  |
| 7d | —»— + PR 1.24, PY 0.25 | 360 | 240 | 59 | >18 | Liquid, sticky | + | Liq.+prec. |  |
| 7e | —»— + PR 1.24, O 1.32, Pe 1.25 | 360 | 240 | 62 | >18 | —»— | + | —»— |  |
| 7f | —»— + S 1.73, M 0.85, PE 1.5 | 360 | 240 | 53 | 7 | Liquid+prec. |  |  |  |
| 7g | —»— + O 1.32, M 0.85, PE 1.5 | 360 | 240 | 35 | 5 | Soft, s. sticky |  |  |  |
| 7h | —»— + PR 1.24, M 0.85, PE 1.25 | 360 | 240 | 69 | >18 | Soft, sticky |  |  |  |
| 7i | —»— + PR 1.24, O 1.32 | 360 | 240 | 42? | >18 | Solid, plumps, sticky |  |  |  |
| 7j | —»— + PY 1.62, O 1.32, PE 2.0 | 360 | 240 | 6? | >18 | Viscous, sticky | ++ | Dark liq.+prec. |  |
| 7k | —»— +PY 1.62, PE 1.0 | 360 | 240 | 13? | >18 | —»— | + | —»— |  |
| 7l | —»— + RE 1.62, PE 1.0 | 360 | 240 | 29 | 13 | —»— | ++ | —»— |  |
| 7m | —»— + V 1.24, PE 0.25 | 360 | 240 |  | 12 | —»— | +++ | Viscous liq. |  |
| 7n | —»— + V 1.24, O 1.32, PE 1.25 | 360 | 240 |  | 10 | —»— | ++ | Visc. clouded |  |

— 5 —

*Table 3.*

| Exp. No | Substances, g of each | Time min. | C° | Color Gardn. | Consistence | Sol. in S+MM | Polymerate peroxide[1]) | radiation |
|---|---|---|---|---|---|---|---|---|
| 8 | PE 5, PA 5.4, F 5.5+M 0.5, PE 0.32 | 20 | 240 | 8 | C. hard, s. sticky | ++ | Hard, clear porous | |
| 8a | —»— + M 0.5, O 0.8, PE 1.0 | 20 | 240 | 6 | —»— | +++ | Hard, some prec. | |
| 9 | —»— + LA 1.0, PE 0.4 | 20 | 240 | 11 | C. hard, c. sticky | +++ | Hard,s.cloud+prec. | Visc. liq. |
| 9a | —»— + LA 1.0, M 0.5, PE 0.72 | 20 | 240 | 7 | C. hards, s. sticky | ++ | Hard, clear | Visc, cloud. |
| 9b | —»— + AF 1.1, PE 0.3 | 20 | 240 | 14 | —»— | +++ | Liquid | Liquid |
| 9c | —»— + AF 1.1, O 1.0, PE 0.8 | 20 | 240 | 11 | C. soft, c. sticky | + | Visc. liq. + prec. | Liquid |
| 10 | —»— + V 1.2, PE 0.25 | 20 | 240 | 10 | —»— | +++ | Hard, c. clear | Liquid |
| 10a | —»— + I 1.5, PE 0.62 | 20 | 240 | | C. hard, clouded | | | |
| 10b | —»— + AF 1.1, M 1.3, PE 1.1 | 20 | 240 | ~14 | C. hard | | | |
| 10c | —»— I 6.1, PE 3.4, F 5.5 | | | | Liquid + prec. | | | |

[1]) Prepared from solution in styrene-methylmethacrylate with aid of benzoyl peroxide catalyst.



Fatty acids are easily esterified compared with rosin acids, and give sometimes give low acid numbers, e.g. exp. 6 and 7, table 2.

The most advantageous effect of the use of fatty acids is, however, that in several cases they make the alkyds soluble in organic solvents, such as styrene-methylmethacrylate 1:1 (S+MM) (compare especially tables 2, 3, and 6). Such solutions at polymerization with benzoyl peroxide in several cases gave satisfactorily hard, even if somewhat clouded polymerates (e.g. 7a, table 2,9 and 10, table 3, XXXVII, XLII, and XLVI–LII). Irradiation with $\gamma$-rays in many cases gave poorer results than the use of benzoyl peroxide.

*Table 4.*

| Exp. No | Substances, g of each | Time min. | C° | Color Gardn. | Consistence | Sol.in S+MM |
|---|---|---|---|---|---|---|
| I | PA 3.7, G 1.24, PE 2.82, F 11.4 | 60 | 210 | 11 | Sticky, cloud. | + |
| II | —»— | 20 | 240 | 11 | Sticky, cloud. l. soft[4]) | — |
| III | —»— +B 2.33 | 20 | 240 | >18 | C. solid, sticky | + |
| IV | PA 5.4, PE 3.4, F 5.5 | 20 | 240 | 9 | Hard, tough[5]) | + |
| IVa | 2g of mixture IV + B 4.0 | 60 | 240 | >18 | Solid | + |
| IVb | 4g of mixture IV + B 2.0 | 20 | 240 | >18 | Hard, brittle | — |
| IVc | 2g of mixture IV + BR 1.0 | 30 | 240 | >18 | —»— | — |
| V | SA 3.64, G 2.27, F 5.5 | 20 | 240 | 11 | Liquid, lumps | — |
| VI | PA 3.7, S 2, G 2.8 | 20 | 240 | 10[1]) | Hard, brittle | — |
| VII | PA 3.7, S 2.0, PE 3.0 | 20 | 240 | 9[2]) | Hard, tough lumps | — |
| VIII | PA 1.9, S 2.0, RE 3.0 + SA 1.3 | 20 | 240 | 4 | —»— | — |
| IX | PA 1.9, S 2.0, SA 1.3, PE 3.6 + F 5.0 | 20 | 240 | 11[3]) | Lumps in part soft | — |
| X | S 2.0, SA 2.6, PE 3.0 | 20 | 240 | 4 | Hard, tough | — |
| XI | S 2.0, SA 1.3, PE 3.3 + F 2.5 | 120 | 240 | 14 | Lumps+liquid | — |
| XII | S 2.0, SA 1.3, PA 1.9, PE 3.2 + F 1.2 | 30 | 240 | 9 | Hard lumps, tough | — |
| XIII | S 2.0, SA 2.6, G 2.7 | 20 | 240 | 4 | Soft, tough lumps | — |
| XIV | S 2.0, SA 2.6, G 1.4, PE 1.5 | 60 | 240 | 4 | —»— | — |
| XV | S 2.0, SA 1.3, PA 1.9, G 1.5, F 1.2 | 60 | 240 | 10 | Hard, rough lumps | — |
| XVI | S 2.0, SA 1.3, PA 1.9, G 1.5, F 1.2 | 60 | 240 | 10 | Hard, tough » | — |
| XVII | S 1.0, PA 1.9, G 1.5, PE 1.6, O 0.8, F 1.2 | 60 | 240 | 8 | —»— yellow lumps | — |
| XVIII | S 1.0, SA 1.3, PA 1.9, G 1.5, PE 1.6, I 1.4, F 1.2 | 75 | 240 | 7 | Yellow, tough particles | — |
| XIX | S 1.0, SA 1.3, I 1.4, PA 1.9, PE 3.0 | 20 | 240 | 1 | Hard, though particles | — |
| XX | S 1.0, SA 1.3, PA 1.9, GL 1.1, PE 3.2, F 1.2 | 70 | 240 | 10 | Tough particles | — |
| XXI | S 1.0, SA 1.3, GL 1.1, PA 1.9, PE 3.0 | 50 | 240 | 1 | Hard, tough » | — |
| XXII | S 1.0, SA 1.3, A 1.2, PA 1.9, PE 3.0 | 60 | 240 | 1 | —»— | — |
| XXIII | S 1.0, SA 1.3, PA 1.9, A 1.2, PE 3.2, F 1.2 | 60 | 240 | 9 | Hard, tough lumps | — |

[1]) Greyish yellow [2]) Light grey [3]) yellow [4]) Acid no 53 [5]) Acid No 71.

*Table 5.*

| Exp. No | Substances, g of each | Time min | C° | Color Gardn. | Consistence | Sol.in. S+MMA |
|---|---|---|---|---|---|---|
| XXIV | S 1.0, SA 2.6, MA 0.8, G 1.4, PE 1.5 | 20 | 240 | 1 | Tough lumps | — |
| XXV | S 1.0, SA 2.6, MA 0.8, G 1.4, PE 1.5 | 30 | 240 | 1 | Tough lumps | — |
| XXVI | S 2.0, SA 2.6, G 1.4, PE 1.5 | 15 | 240 | 1 | Hard,tough lumps,colorl. | — |
| XXVII | S 2.0, SA 2.6, G 1.4, PE 1.5 | 20[1]) | 240 | 1 | —»— | — |
| XXVIII | S 2.0, SA 2.6, PE 1.5 | 8[1]) | 200 | 1 | Soft, tough —»— | — |
| XXIX | S 2.0, SA 2.6, PE 1.6, G 1.5, F 1.2 | 10[1]) | 210 | 9 | Soft, tough oily particl. | — |
| XXX | SA 4.3, G 1.5, PE 1.6, F 1.2 | 20 | 210 | 10 | —»— | — |
| XXXI | SA 4.3, G 1.5, PE 1.6, F 1.2 | 30 | 200 | 9 | Liquid | — |
| XXXII | SA 3.65, PE 3.4, F 5.5 | 20 | 220 | 8 | Hard, tough, oily part. | — |
| XXXIII | SA 1.8, PE 1.7, G 1.5, F 5.5 | 30 | 240 | 7 | Liquid+gel | + |

[1]) Using addition of xylene, in order to remove water.

Further, the following conclusions seem to be justified:

Phthalic acid anhydride can be at least partly (exp. XV, XVI, XIX, XXI, XXII, table 4, XLII, XLIX, LIII, LIV, table 6, or even totally substituted by succinic anhydride, exp. XXVI, XXVII, table 5.

Oxalic acid can be used as an acidic component in alkyds (exp. XLII and XLV, table 6).

If both pentaerythritol and succinic anhydride are used, the alkyd is insoluble in styrene-methylmethacrylate, though fatty acid is used (exp. IX, XI, XII, XV, XVII, XVIII, XX, XXIII, table 4, XXIX – XXXII, table 5, and XXXV, table 6), but if lactic acid is used in addition, the alkyd is soluble in the solvent mixture (exp. XLIX, table 6).

Use of benzyl lignin in one case (exp. III, table 4) made the alkyd soluble in the solvent mixture above named, but the color is rather dark.

The alkyds prepared without fatty acids or benzyl lignin in general were colorless or white.

*Grants from Raf. Haarlan Säätiö are gratefully acknowledged.*



*Table 6.*

| Exp. No | Substances, g of each | Time min. | C° | Acid No | Color Gardn. | Consistence | Sol. in S+MMA | Polymerate[1]) |
|---|---|---|---|---|---|---|---|---|
| XXXIV | SA 1.8, PA 2.7, G 3.0, F 5.5 | 20 | 240 | | 8 | Soft, sticky | +++ | L. yellow, c. hard |
| XXXV | SA 1.8, PA 2.7, G 1.5, PE 1.7, F 5.5 | 25 | 240 | | 10 | Hard tough lump+liq. | — | |
| XXXVI | SA 2.4, PA 1.8, G 3.0, F 5.5 | 20 | 240 | | 8 | Liq.+gel. | + | L. yellow, Cloud[2]) |
| XXXVII | SA 1.2, PA 3.6, G 3.0, F 5.5 | 20 | 240 | | 10 | Viscous, sticky | +++ | L. yellow, c. hard, cloud |
| XXXVIII | SA 2.0, PA 3.7, G 2.8 | 15 | 140 | | 1 | Though lumps | — | |
| XXXIX | SA 1.8, PA 2.7, G 2.5, F 5.5 | 40 | 240 | | 11 | Soft, sticky | +++ | |
| XL | SA 1.8, PA 2.7, G 3.0, F 5.5 | 40 | 240 | | 12 | In part rubberlike | + | |
| XLI | PA 2.80, L 2.11, G 1.37, Xy 0.25 | 120 | 255[3]) | | 18 | C. hard | ++ | Brown, clear [4]) |
| XLII | SA 1.8, PA 2.7, O 0.32, G 3.0, F 3.5 | 20 | 240 | 68 | 10 | Soft, clear, l. yellow | +++ | C. hard, cloud, l. yellow |
| XLIII | SA 3.6, O 0.32, G 3.0, F 3.5 | 25 | 240 | | 8 | Soft lumps+oil | — | |
| XLIV | SA 3.6, O 0.32, G 3.0, F 3.5 | 25 | 240 | | 8 | —»— | — | |
| XLV | SA 1.8, PA 2.7, O 0.32, G 3.0, F 3.5 | 20 | 240 | | 9 | Soft, tough lumps | ++ | Hard, alm. clear [4,5]) |
| XLVI | PA 5.4, LAc 1.8, G 0.65, PE 3.4, F 5.5 | 20 | 240 | 55 | 11 | Soft | +++ | L. yellow, c. hard |
| XLVII | PA 5.4, LAc 1.8, G 3.7, F 5.5 | 20 | 240 | 71 | 10 | Soft, sticky | +++ | —»— hard, s. cloud |
| XLVIII | PA 5.4, LAc 1.8, PE 4.1, F 5.5 | 20 | 240 | 82 | 11 | Liquid, sticky | +++ | —»— |
| XLIX | SA 0.5, PA 5.4, LAc 0.9, PE 4.1, F 5.5 | 20 | 250 | 73 | 11 | C. hard | +++ | —»— |
| L | SA 0.5, PA 5.4, LAc 0.9, G 3.7, F 5.5 | 20 | 240 | 77 | 11 | Soft, sticky | +++ | —»— |
| LI | SA 1.4, PA 2.7, LAc 2.55, G 3.7, F 5.5 | 30 | 240 | 42 | 11 | —»— | +++ | L. yellow, c. hard, clouded |
| LII | SA 1.4, PA 2.7, LAc 2.55, G 4.0, F 5.5 | 20 | 240 | 46 | 11 | —»— | +++ | C. coloured, hard, s. clouded |
| LIII | SA 1.4, PA 2.7, LAc 2.55, G 3.7, I 1.6 | 20 | 240 | 107 | 1 | C. hard, tough, clear | — | |
| LIV | SA 1.4, PA 2.7, O 1.27, G 3.7, I 1.6 | 20 | 240 | >73 | | White, though, lumps | — | |

[1]) Prepared from solution in styrene-methylmethacrylate with aid of benzoyl peroxide catalyst.

[2]) Comparatively hard, alkyd not entirely dissolved.

[3]) First heating of L+G 120 min. at 255°; then addition of PA and heating 72 min. at 200°, at last addition of xylene and heating 60 min. at 170°.

[4]) Part of the alkyd undissolved.

[5]) Light yellow.

List of abbreviations in the tables 1—6.

A = adipic acid — AF = acidic, water soluble fraction from demethylated kraft black liquor — B = benzyl lignin — BR = benzyl lignin rebenzylated — E = ethylene glycol — F = fatty acid fraction (content of rosin acids 2 %) from distilled tall oil — G = glycerol — GL = glutaric acid — I = isophthalic acid — L = linseed oil — LAc = lactic acid — M = maleinic acid — MA = maleinic acid anhydride — MM = methyl metacrylate — O = oxalic acid — OL = oleinic acid — PA = phthalic acid anhydride — PE = pentaerythritol — PR = protocatechuic acid — PY = pyrocatechol — R = crystallized rosin acid mixture from distilled tall oil — RE = resorcinol — S = succinic acid — SA = succinic anhydride — SO = sorbitol — St = monostyrene — V = vanillic acid — VA = vinylacetate — Xy = xylene.

c = comparatively
L = light liq. = liquid
prec. = precipitate
s = somewhat

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# Microbial Action on Lignosulfonates

*Johan-Fredrik Selin and Veronica Sundman*

*Department of General Microbiology, University of Helsinki/Helsingfors, Finland*

*Summary*

A mixed microbial population consisting of bacteria and protozoa was cultured in a liquid medium which contained a lignosulfonate preparation, Peritan-Na, as the sole source of energy. By means of ultrafiltration, thin layer chromatography and ether extractions it was shown that only components of low molecular weight (mol.wt. < 1,000) could be utilized by the microbes as sources of energy. True lignosulfonates of higher molecular weight were polymerized and darkened but did not support microbial growth.

## *Introduction*

In a previous paper (11) we showed that a mixed population of micro-organisms was able to grow in a liquid medium in which a sugar-free lignosulfonic acid preparation served as the sole source of energy. During growth, changes were found to occur in the molecular weight distribution, as measured by means of gel permeation chromatography. However, because the micro-organisms only grew satisfactorily on fractions of relatively low molecular weight, < 10,000, the question remained whether true lignosulfonates supported microbial growth, or whether it was impurities of low molecular weight that were responsible for the growth noted. In this paper we shall discuss some of the experiments performed with the aim of finding an answer to this question.

## *Materials and methods*

*Lignosulfonate.* The lignosulfonate preparations used were Peritan-Na obtained from Norcem AS, Oslo, Norway, and fractions prepared from this product by passing it through Amicon Diaflo ultrafilters covering different fractionation ranges.

*Model compounds.* All model compounds were commercial preparations of analytical grade.

*Culture media.* A mineral-vitamin solution, the composition of which is shown in Table I, was supplemented with about 1 % (w/v) of a lignosulfonate preparation. The media were dispensed in 20-ml portions into 250-ml conical flasks, weighed, and sterilized by autoclaving.

*Table I.* Composition of the base medium.

| Component | Amount | |
|---|---|---|
| $NH_4Cl$ | 2.0 | g |
| $MgSO_4 \cdot 7H_2O$ | 0.3 | ,, |
| NaCl | 0.1 | ,, |
| $CaCl_2 \cdot 2H_2O$ | 0.01 | ,, |
| $FeCl_3 \cdot 6H_2O$ | 0.01 | ,, |
| Sörensen's M/15 phosphate buffer, pH 6.5 | 300.0 | ml |
| Vitamin solution * | 5.0 | ,, |
| Distilled water | 695.0 | ,, |

* 10 mg each of thiamine, pyridoxine, calcium pantothenate, nicotinic acid and p-aminobenzoic acid, 2 mg of folic acid, 40 $\mu g$ of vitamin $B_{12}$, and 20 $\mu g$ of biotin in 200 ml of water.

*Micro-organisms.* The microbial culture was the same mixed population of bacteria and protozoa, designated "H", which was previously described (11). The cultures were incubated on a rotary shaker for 5 days at 28°. After incubation the weight of the flasks was made up to the original by addition of distilled water. The cells were harvested by centrifugation, the amount of remaining lignosulfonate and the color were determined from the supernatant, and the amount of protein from the washed cell sediment.

*Determination of lignosulfonates.* Lignosulfonates were determined colorimetrically at 440 nm by the nitroso method of JAYME and POHL (5). Unfractionated Peritan-Na was used as a standard.

*Determination of cell protein.* The amount of cell protein was measured according to the method of LOWRY et al. (7), with the modifications already described (11), and with Kabi serum albumin as a standard.

*Color.* The color of the medium was estimated as the absorbance at 500 nm.

*Thin layer chromatography.* The low-molecular weight components of a fraction with an upper mol.wt. limit of 1,000 were characterized by means of thin layer chromatography. The

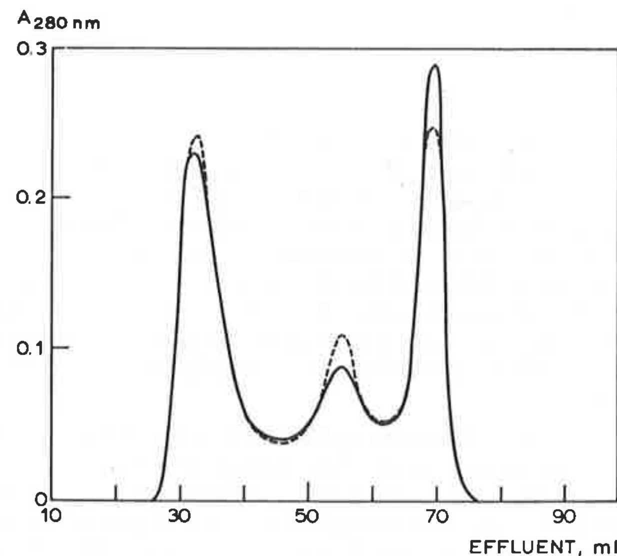


plates were sheeted with Merck Kieselgel $HF_{254}$ with a layer thickness of 0.25 mm. For better separation the plates were buffered with phosphate buffers to pH 6 or 7. The solvent systems used were butanol saturated with water, butanol-ethanol-water (5:3:1) and chloroform-benzene-ethanol (120:40:25). The spots were detected by irradiating the plates with ultraviolet light of wavelengths 254 or 360 nm, or by spraying the plates with the phenol reagents diazotized sulfanilic acid or p-nitroaniline and also other widely used spraying reagents (4).

*Gel permeation chromatography (GPC.)* The relative molecular weight distributions were determined by means of GPC on Sephadex G-25 and G-50 gels in columns 9 mm in diameter and 560 mm high. The transmission at 280 nm of the effluent was automatically recorded with a Uvicord II UV absorptiometer from LKB-Produkter AB, Sweden. The values were transformed to absorbance values for the figures in this paper.

## *Results*

In Table II are listed some data from experiments with different ultrafiltered fractions of Peritan-Na. It is obvious that the mixed culture of bacteria and protozoa requires compounds of low molecular weight for growth. Thus, in the fraction with a molecular weight of less than 1,000 the cell protein yield was almost ten times as high as the yield in the next fraction, mol.wt. 10,000 – 1,000 (2.89 % *vs.* 0.32 %). Moreover, there was a remarkable coloration of the medium with the fraction of mol.wt. 10,000 – 1,000. As earlier shown (11), this coloration is connected with polymerization. Comparison of the figures for the relative color increase (Table II) shows that this was more than ten times as strong in the fraction 10,000 – 1,000 as in the fraction with mol.wt. $< 1,000$ (864 *vs.* 80). The relative color increase is calculated as the ratio between the color increase in percent and the cell protein yield in percent. That the coloration (= polymerization) preferably occurs in the fraction of mol.wt. 10,000 – 1,000 is also seen from the GPC curves in Fig. 1 and 2. Polymerization of the compounds is negligible in the fraction with mol.wt. $< 1,000$ (Fig. 1), but very strong in the fraction with mol.wt. 10,000 – 1,000 (Fig. 2). It should also be noted that the nitroso method is more sensitive to polymerization, which implies a decrease in phenolic hydroxyl groups, than to a real decrease of lignosulfonates due to utilization (cf. the discussion). Hence the relatively small decrease, 13 %, in fraction $< 1,000$ compared to the 24.7 % decrease in fraction 10,000 – 1,000 (Table II).



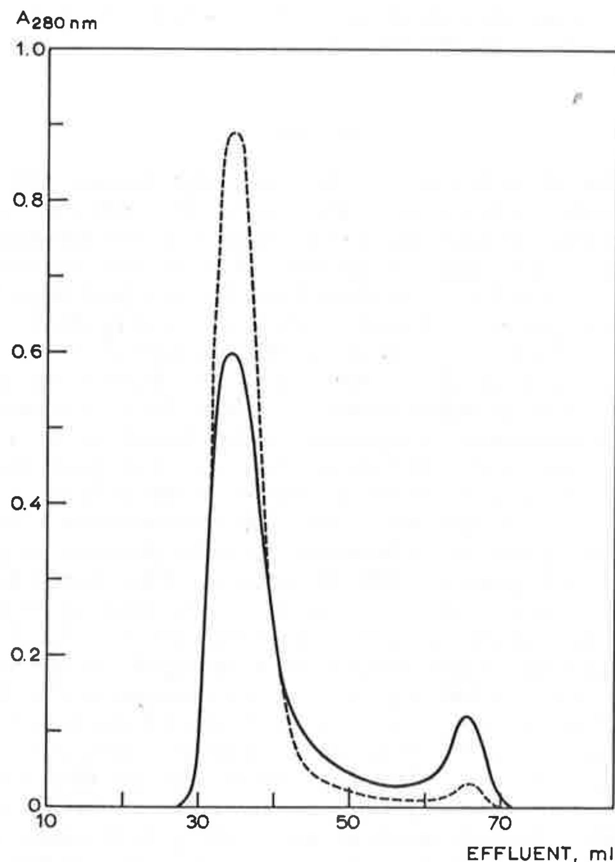




*Fig. 1.—2.* GPC-curves of samples of growth media with Peritan-Na fractions of mol.wt. <1,000 (Fig. 1) and 10,000—1,000 (Fig. 2) as sole source of energy. Elution with water on Sephadex G-25 gel.
——— sterile control
– – – – cell-free supernatant after growth



*Table II.* Cell protein yield, decrease of lignosulfonate and relative color increase after growth. The figures are means of triplicates.

| Carbon source of medium | Protein yield in percent of added lignosulfonate | Percentile decrease of lignosulfonate during growth | Relative color increase |
|---|---|---|---|
| Unfractionated Peritan-Na | 0.61 | 18.0 | 375 |
| Ultrafiltrate | | | |
| <10,000 | 1.70 | 39.5 | 229 |
| 10,000—1,000 | 0.32 | 24.7 | 864 |
| <1,000 | 2.89 | 13.0 | 80 |

Thin layer chromatography with the solvent system chloroform-benzene-ethanol (120:40:25) and with the plates buffered to pH 7.0 revealed that the fraction with mol.wt. < 1,000 could be divided into 12 distinct spots in addition to a strong dark one which remained at the site of application. After growth, only one of the migrating spots remained (Table III). Since the spots stained with diazotized sulfanilic acid they were probably phenolic compounds of relatively low molecular weight. And it is evident that these are utilized by the microbes. In the other systems used, the general picture was almost the same, but the separation was not so good, "tailing" occurred, and only 4—6 spots could be seen in a sterile control sample.

All the solvent systems gave spots with $R_f$ values and colors that were in very good agreement with those of the following reference substances: p-hydroxybenzoic acid, vanillic acid, vanillin and α-conidendrin. Separation of vanillin and α-conidendrin was achieved in the system ethyl acetate-benzene (45:55). In all probability acetovanillone and sulfonated derivatives of the above-listed and other related compounds were also present (1, 3, 6, 8, 9, 10). In order to show that it is possible for the mixed microbial culture to grow on these simple phenolic compounds, we prepared the usual growth medium and added 20 mg/100 ml of either p-hydroxybenzoic acid, vanillic acid or vanillin as the sole source of energy. As a fourth medium we used a mixture of these three model compounds and α-conidendrin, 8.0 mg/100 ml of each. The results are listed in Table IV. The mixed population grew well and was capable of utilizing more than 90 percent of the added phenols. No color due to polymerization could be detected in the samples after incubation, nor could any changes in the composition of the population be observed on examining it under the microscope.

The amount of ether-soluble components present and the growth on these were measured in a diethyl ether extract of an acidified sample of a fraction with mol.wt. < 10,000. Such

*Table III.* Microbial utilization of low-molecular weight phenolic compounds in Peritan-Na fraction of mol.wt. <1,000 as shown by thin layer chromatography of growth medium. Plates: 0.25 mm Kieselgel $HF_{254}$ buffered to pH 7.0. Solvent system: $CHCl_3$-Bz-EtOH (120:40:25). Spraying reagent: Diazotized sulfanilic acid.

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sterile medium: | 0.00, | 0.07, | 0.15, | 0.20, | 0.24,[1]) | 0.28,[2]) | 0.33, | 0.37, | 0.48, | 0.56, | 0.66, | 0.77,[3]) | 0.80[3]) |
| Centrifugate of medium after growth: | 0.00, | | | | | | 0.32 | | | | | | |
| Reference compounds | | | | | | | | | | | | | |
| p-Hydroxybenzoic acid: | | | | | 0.25 (yellow) | | | | | | | | |
| Vanillic acid: | | | | | | 0.28 (orange) | | | | | | | |
| Vanillin: | | | | | | | | | | | | 0.78 (reddish brown) | |
| α-Conidendrin: | | | | | | | | | | | | 0.79 (brown) | |
| Acetovanillone: | | | | | | | | | | | | 0.78 (brown) | |

[1]) yellow
[2]) orange
[3]) The last two spots are diffuse and apparently composed of several ones in the actual solvent system.
All other spots are brown to reddish brown.



*Table IV.* Microbial growth on simple phenolic model compounds.

| Carbon source of medium | $A_{280}$ nm of sterile medium | Percentile decrease in $A_{280}$ nm during growth | Protein yield in percent of added C-source |
|---|---|---|---|
| 1. p-Hydroxybenzoic acid, 0.02 % | 4.85 | 93.0 | 18.7 |
| 2. Vanillic acid, 0.02 % | 6.30 | 93.9 | 15.2 |
| 3. Vanillin, 0.02 % | 14.25 | 98.0 | 19.5 |
| 4. 1+2+3+α-conidendrin, 0.008 % of each | 10.40 | 92.7 | 14.9 |

ether-soluble components would be expected to be simple phenols and phenolic acids. The sample to be extracted was dissolved in water at about 1 % concentration. After extraction, the ether remaining in the water phase was distilled off, and inorganic salts, vitamins and water were added to make up the original volume and the correct growth medium composition. The ether extract was treated in a similar way, and was brought up to the same volume. The concentration of the ether-soluble

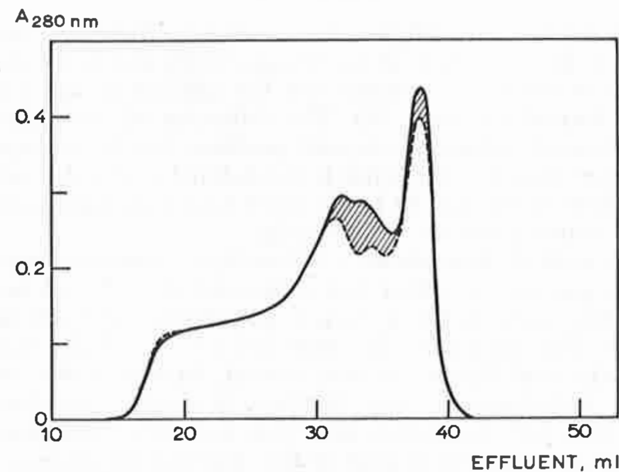



*Fig. 3.* GPC-curves of untreated and ether extracted samples of a Peritan-Na fraction of mol.wt. <10,000. Elution with water on Sephadex G-50 gel. The hatched area, 8 percent of the area of the untreated sample, represents the amount dissolving in ether during extraction.
———— untreated sample
— — — — extracted sample

components was calculated as the difference in the concentrations of the untreated and extracted samples (*cf.* Table V). The amount extracted was 8 percent of the untreated sample. The same result is obtained on measuring the hatched area between the GPC curves of Fig. 3. In spite of the low concentration of organic compounds, the microbes grew well on the extract, the yield of cell protein amounted to 19.4 per cent of that obtained on the unextracted sample. *viz.* 0.44 mg/20 ml *vs.* 2.28 mg/20 ml (Table V). The utilization of the "lignosulfonates" was likewise much more efficient in the extract than in the unextracted sample (percentile protein yield 2.93 *vs.* 1.21). No color due to polymerization could be detected with the extract.

*Table V.* Effect of ether extraction upon the microbial growth on Peritan-Na fraction of mol. wt. <10,000.

| Carbon source of medium | Concentration, percent, of lignosulfonate in growth medium | Cell protein yield | |
|---|---|---|---|
| | | mg/20 ml | percent of added C-source |
| Unextracted fraction | 0.940 | 2.28 | 1.21 |
| Ether extracted » | 0.865 | 1.83 | 1.06 |
| Ether extract | 0.075 | 0.44 | 2.93 |

## *Discussion*

The recalcitrance of lignosulfonic acids to biological degradation is a well-known fact. It is perhaps chiefly due to the complex structure of the lignin skeleton, but the sulfonic groups may also play an important part (12). The difficulty of obtaining pure and uniform preparations is a great problem, too. Some impurities may always remain. And what is the definition of a lignosulfonic acid? Where is the line to be drawn between lignosulfonic acids and sulfonated phenolic compounds?

In this work we have shown that in a lignosulfonate preparation only components of rather low molecular weight, $>1,000$, can be directly utilized by a mixed population of bacteria and protozoa. But although the microbes almost wholly failed to grow on the next higher fraction, mol.wt. 10,000 – 1,000, changes could be noted even in this fraction. A strong coloration connected with polymerization occurred, and this "humification", too, must be regarded as part of the degradation process.

Methods of demonstrating degradation and other changes in the lignosulfonates are still in need of improvement. In some preliminary experiments we found that the nitroso values are a direct measure of the phenolic hydroxyl groups. The percentile decreases in the nitroso values due to microbial growth, were



exactly the same as the decreases in the phenolic hydroxyl contents measured with the difference spectrogram method as described by WEXLER (13). Decreases in the hydroxyl group content occur mainly during polymerization processes. Upon microbial degradation the hydroxyl content may remain fairly constant owing to the combined effects of demethylation of methoxyl groups and dehydroxylation. This is one explanation of the fact that the differences noted in lignosulfonic acid concentration are usually rather small, whereas much greater differences are always found when there is coloration (= polymerization) of the medium. In this connection, the work of GASPARIČ (2) must also be recalled. This researcher has shown that it is not nitroso derivatives but nitro compounds that are formed when the "nitroso" method is applied to phenols.

## *Acknowledgment*

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## Litteratur

**Lennart Eberson:** *Organisk kemi.* Almqvist & Wicksell 1970
596 sidor.

Enligt företalet är boken avsedd för lågstadieundervisningen i organisk kemi vid universitet och andra högskolor. Dess innehåll förefaller dock att vara något vidlyftigare än vad vi i Finland brukar anse höra till en grundkurs i organisk kemi.

Författaren har rätt mycket avvikit från den traditionella indelningen av materialet i en kurs av denna typ. De första nio kapitlena behandlar allmänna begrepp såsom nomenklatur, stereoisomeri, energetik, kinetik och reaktionsmekanism. Författaren har genomgående försökt använda sig av så korrekta och modärna uttryck som möjligt, även om han därvid avviker från vad i allmänhet är brukligt i organisk kemisk litteratur. Så användes kJ i stället för kcal, karbokatjon i stället för karboniumjon och semijonisk binding i stället för semipolär binding. Mot detta är ju ingenting i princip att invända, men det hade kanske varit på sin plats att kommentera dessa användningar litet utförligare. Så är ju t.ex. begreppet karboniumjon helt dominerade i den engelskspråkiga litteraturen, varför svårigheter lätt uppstår för den som lärt sig att tala om karbokatjon.

Däremot kan jag icke inse varför författaren använder enheten Å för att ange våglängder för ljusabsorption i det ultravioletta och synliga området. I den organisk kemiska litteraturen används ju nästan uteslutande nm (tidigare m$\mu$), som ju också är den riktiga enheten.

I den andra delen av boken behandlas sedan de olika organiska ämnesklasserna i ganska traditionella ordning, men endast med hänsyn till deras reaktioner. Detta leder naturligtvis till att framställningsmetoderna för en viss typ av förening behandlas i samband med utgångsmaterialets reaktioner och således finnes utspritt på en massa olika ställen i boken. Att detta är en svaghet har författaren naturligtvis också insett, och han har kompenserat detta genom att införa ett skilt kapitel om syntes. I detta har han i tabellform uppfört de viktigaste syntetiska metoderna med en hänvisning till det ställe i boken där reaktionen behandlas utförligare. Dessa tabeller är säkert också för den längre hunna organikern av stort värde, då han hastigt vill orientera sig om vilka möjligheter som står till buds för en viss syntesgång.

Den tredje och sista delen behandlar tillämpad organisk kemi. Att behandla denna på drygt 50 sidor är ej lätt, men det förefaller som om författaren skulle ha lyckats väl vid avvägningen av vad som bör tagas med.

Bokens utstyrsel är av synnerligen hög kvalitet, ja man frågar sig faktiskt om den ej, med tanke på den läsekrets till vilken boken vänder sig, kunde ha varit något enklare.

Att få till stånd en lärobok, helt utan tryckfel är väl en utopi. Också i denna bok finnes sådana, även om de ej är många. De flesta är helt uppenbara, men några kan nog ge läsaren litet huvubry. Så har på s. 126 olikhetstecknena för racemiseringshastighetens beroende av substituenten blivit vända åt fel håll. På s. 155 har vid framställningen av nitrobenzenets resonans den andra och den sista gränsformeln blivit identiska. Dessutom framgår ej den ena NO-bindningens semipolära (eller enligt författaren semijoniska) natur. Detta gäller för övrigt nitrogruppen på ett antal andra ställen i boken också (ss. 290, 398, 410), medan den är angiven på en del ställen (ss. 31, 197, 211).

Som helhet betraktat förefaller boken att synnerligen väl fylla sin uppgift som en introduktion till modärn organisk kemi.

*Jarl Gripenberg*

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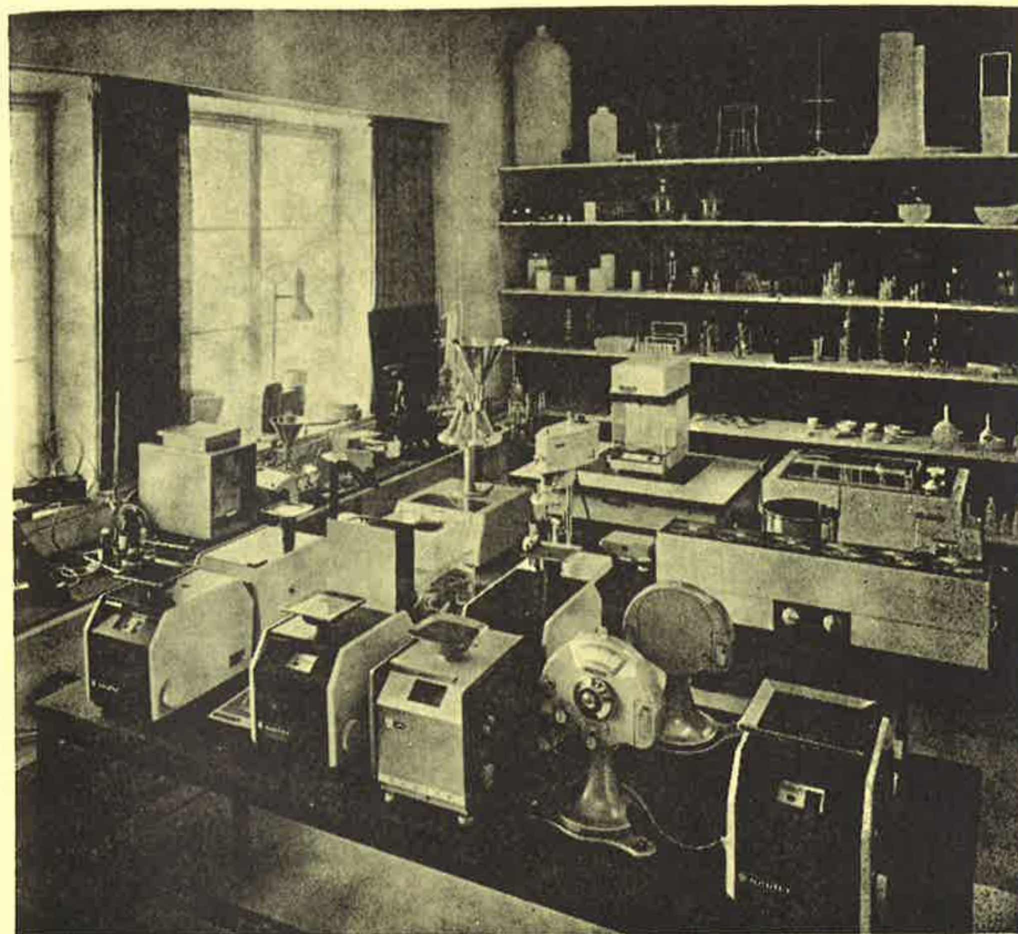

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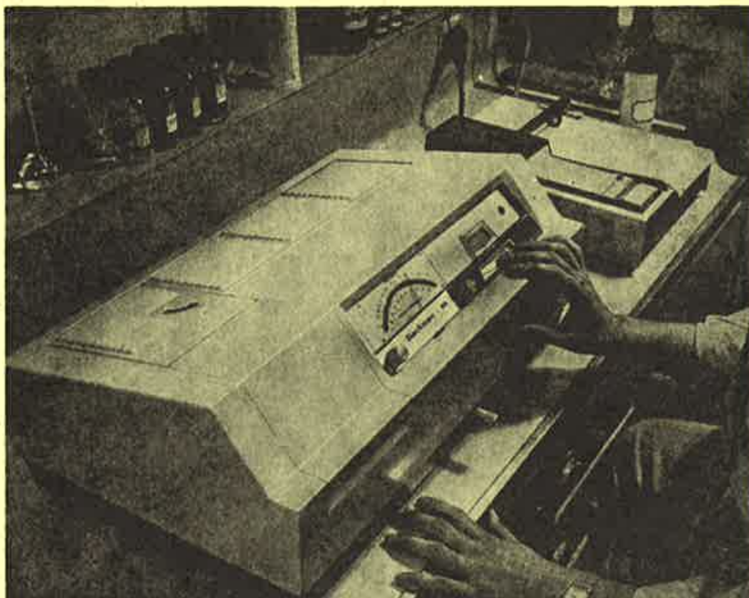

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