LVII årg. 1948 N:o 1—2 LVII vuosik.

FINSKA KEMISTSAMFUNDETS MEDDELANDEN

SUOMEN KEMISTISEURAN TIEDONANTOJA

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HELSINGFORS — HELSINKI
FINLAND — SUOMI

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Finska Kemistsamfundet — Suomen Kemistiseura

Berättelse

över

Finska Kemistsamfundets verksamhet under år 1947.

Avgiven vid mötet den 17 februari 1948.

Samfundets möten ha hållits den 12 februari, den 19 mars, den 6 maj, den 3 oktober, den 11 november och årsmötet den 10 december. Med undantag för mötet den 6 maj, då prof. L. Meitner var inbjuden föredragare, ha mötena hållits under de i stadgarna bestämda månaderna. Mötena den 6 maj och 3 oktober höllos i Skogshuset, de övriga i Ständerhuset. Närvarande ha varit i medeltal 19 medlemmar mot 20 föregående år. Styrelsen har sammanträtt 6 gånger.

Laudaturstudenterna vid Helsingfors Universitet samt kemistuderandena vid Tekniska Högskolan ha inbjudits till samfundets möten.

Programmen ha upptagit följande föredrag och meddelanden:

Derrik Ekström: Moderna laboratoriedestillationskolonner.

H. v. Euler: Nya rön om nukleinsyrornas kemiska egenskaper och biologiska roll.

Nils Gralén: Äro konstfiber bättre än naturliga fibrer?

Bengt Grotenfelt: Demonstration av en transportabel Geiger-Müller apparat.

Ch. Gustafsson: Några erfarenheter om tallolja och sulfatterpentin som råvara inom den kemiska industrin.

L. Meitner: Ueber die verschiedenen Spaltungsmöglichkeiten des Urans bei Bestrahlung mit Neutronen.

B. Nybergh: Redogörelse för klorexplosionen vid Raumo sulfitcellulosafabrik.

John Palmén: Chemical Societys 100-årsjubileum.

L. Simons: Intryck från fysikerkongressen i Paris samt från England.

W. Wahl: Nya metoder för industriell framställning av syre.

Vårexkursionen anordnades den 30 maj tillsamman med Tekniska Föreningens Avdelning för Kemi till A. B. Karl Fazers fabriker i Helsingfors.

Tillsamman med Suomalaisten Kemistien Seura har samfundet inbjudit prof. L. Meitner, som höll sitt föredrag den 6 maj, samt sin hedersmedlem, nobelpristagaren, prof. H. von Euler, som höll sitt föredrag den 3 oktober. Vidare har samfundet inbjudit docenten, fil.dr Nils Gralén från Textilforskningsinstitutet i Göteborg, som höll sitt föredrag den 11 november. Tekniska Föreningens Avdelning för kemi hade inbjudit samfundets medlemmar att den 1 april åhöra ett föredrag av fil.mag. Stig Lindroth, Chalmers Tekniska Högskola, Göteborg, över ämnet »Om glasets struktur». Samfundets medlemmar ha likaså varit inbjudna att deltaga i det konstituerande mötet för det nya samfundet för litteraturtjänst i Finland.

Viceordföranden, prof., friherre John Palmén representerade samfundet vid Chemical Society's 100-årsjubileum den 15—17 juli i London.

Samfundet har till sina representanter i Delegationen för Finlands Kemister, förutom ordföranden och sekreteraren, för en tid av fem år framåt utsett professorerna W. Qvist, J. Palmén och W. Wahl samt till medlemmar av Acta Chemica Scandinavicas redaktionskommitté för Finland professorerna K. Buch och P. Ekwall, varjämte samfundets sekreterare, mag. O. Ojala fungerat som redaktionskommitténs sekreterare. Under året ha sex nummer av tidskriften ifråga hunnit utkomma med ett sammanlagt sidoantal av 604, och hela årgången (10 nr.) beräknas ha utkommit i februari/mars 1948. Undervisningsministeriet har för 1947 beviljat samfundet och Suomalaisten Kemistien Seura ett gemensamt anslag om 300.000 mk för bestridande av Finlands andel i utgifterna för nämnda tidskrift.

Kemistförbundet i Finland hade insänt en skrivelse betr. laboratorie- och laborantbenämningarna, och omfattade samfundet nämnda förbunds uppfattning i saken.

Vid ett möte den 10 januari av representanter för landets ingeniörs- och arkitektsammanslutningar diskuterades frågan om dessa föreningars inbördes samarbete. En kommitté tillsattes för att vidare behandla frågan och denna tillställde samfundet ett den 5 september daterat förslag till bildande av en delegation för nämnda sammanslutningar samt anhöll om samfundets utlåtande i saken. Samfundets styrelse har emellertid icke t. v. velat fatta ståndpunkt i saken, då samfundet är ett sådant av rent vetenskaplig natur.

Av Meddelanden har utkommit N:ris 1—4, 1946 samt 1—2, 1947. Tidskriftsutbytet är fortfarande rätt begränsat, men arkivarien har under året erhållit befogenhet att skrida till de åtgärder i detta hänseende, som kunna anses vara påkallade.

Priset för 1947 ur bergsrådet Alfthans fond för premiering av uppsatser i kemi tilldelades prof. Torsten Storgårds för hans artikel »Kemiska problem på smörtillverkningens område».

Under året ha följande nya medlemmar invalts: dipl.ing. Alexander Bassin, fil.mag. Bengt Kihlman, dipl.ing. Håkan Lühr, fil.mag. Veronica Sundman, dipl.ing. Christina Rönnholm, dipl.ing. Irma Nyberg, dipl.ing. Marcel Lehtonen, laboratorieföreståndare Runar Hasselström, fil.mag. John Tuderman samt dipl.ing. Derrick Ekström.

Tre medlemmar ha avgått, medan följande medlemmar avlidit: direktör, fil. mag. A. Backman, apotekaren T. A. J. Jääskeläinen, prof. E. J. Salmi och fil.dr A. Schwalbe.

Medlemsantalet har ökat med 8 och utgjorde vid årets utgång 312.

Styrelsen har haft följande sammansättning:

Ordförande: fil.dr Erik Ehrnrooth,
Viceordförande: prof., friherre John Palmén,
Övriga styrelsemedlemmar: prof. K. Buch, fil.dr C. W. Chydenius, ing. R. Holmström, fil.dr B. Nybergh, prof. L. Simons, fil. dr T. Smedslund samt

Sekreteraren: fil.mag. Onni O. Ojala.
Redaktör: sekreteraren,
Arkivarie: ing. Anna Grönvik,
Kassör: fil.mag. C. Fogelberg,
Revisorer: ing. S. Petander och mag. Albert Backman med fil.kand. Svante Nordström som suppleant.

På styrelsens vägnar:

Onni O. Ojala.

Möte — Kokous.
17. II. 1948.

§ 1. På enhälligt förslag av styrelsen invaldes till medlem av samfundet fil.mag. Nils Anders Aschan, föreslagen av mag. Bröderman och mag. Lagerbohm.

§ 2. Årsberättelsen och bokslutet samt revisionsberättelsen föredrogos varefter vederbörande beviljades ansvarsfrihet.

§ 3. Ordföranden meddelade om de åtgärder som vidtagits för de finska kemistsamfundens anslutning till den internationella unionen.

§ 4. Då prof. Palmén i sin egenskap av samfundets ordförande är självskriven medlem av Delegationen för Finlands Kemister utsågs prof. K. Buch till samfundets representant under år 1948 i nämnda delegation, då samfundet sålunda under 1948 representeras av professorerna Buch, Qvist och Wahl samt ordföranden och sekreteraren.

§ 5. Sekreteraren meddelade att samfundet uppvaktat sin hedersmedlem prof. Hans von Euler telegrafiskt på hans 75-årsdag samt att viceordföranden och sekreteraren uppvaktat prof. Toivonen på hans 60-årsdag.

§ 6. Prof. K. Buch höll härefter ett föredrag om »*Några drag ur atomlärans inverkan på kemins utveckling*». I den efterföljande diskussionen deltogo ing. Nyberg och dr Ehrnrooth samt föredragaren, till vilken ordföranden sedan framförde samfundets tack.

§ 7. Ordföranden hyllade i anslutning till årsberättelsen minnet av de under året avlidna medlemmarna fil.mag. Albert Backman, apotekare T. A. J. Jääskeläinen, prof. E. J. Salmi och fil.dr A. Schwalbe.

Möte — Kokous.
16. III. 1948.

§ 1. Ordförande öppnade mötet och meddelade att till sekreterare vid mötet kallats fil.mag. Holger Lönegren då samfundets ordinarie sekreterare på grund av utrikesresa var förhindrad att närvara.

§ 2. Ordföranden meddelade att prof. J. L. Simonsen från London den 12—13 april i Helsingfors skulle hålla tvenne föredrag.

§ 3. Ordföranden meddelade att Delegationen för Finlands Kemisters stadgar granskats i och för inregistrering i föreningsregistret, samt att ansökan om medlemskap för delegation i International Union of Chemistry gjorts.

§ 4. Samfundet godkände styrelsens förslag att till revisorer i Delegationen för Finlands Kemister utse dr W. Forsman med dr H. Tötterman som suppleant.

§ 5. Ordföranden meddelade att samfundet ansökt om tryckningsbidrag för Meddelandena för år 1948.

§ 6. Ordföranden meddelade att samfundets aprilmöte kommer att hållas i samband med prof. Simonsens föredrag den 12—13 april.

§ 7. Ordföranden meddelade att uppgiften om samfundets vårexkursion skall givas i vanlig ordning.

§ 8. Upplästes Suomalaisten Teknikkojen Seuras inbjudan till föredragstillfället och årsmötet den 17 april 1948.

§ 9. Fil.mag. Kurt Lupander höll ett föredrag om »*Bergshanteringens utveckling*» i Finland under senaste decennium. Ordföranden avtackade föredragshållaren varefter hrr Wahl, Ehrnrooth, Palmén, Forsman och föredragshållaren yttrade sig i anledning av föredraget.

Möte — Kokous.
12. IV. 1948.

§ 1. På enhälligt förord av styrelsen invaldes följande nya medlemmar: dipl.ing. Stig Landgren, föreslagen av ingeniörerna H. Nyberg och H. von Koskull, dipl.ing. Rolf Lindahl, föreslagen av prof. Palmén och mag. Lönegren samt dipl.ing. Lars Johan Aschan föreslagen av B. Björkenheim och dr. Smedslund.

§ 2. Ordföranden meddelade att samfundet av Suomalaisten Kemistien Seura inbjudits att åhöra ett föredrag som den 19 april hålles av prof. Geiger-Huber, Schweiz över ämnet »Hormonale Regulierung des Pflanzenwachstums» samt på inbjudan av Tekniska Högskolan att den 19 april åhöra ett föredrag av prof. B. Groth över ämnet »Något om den nyare utvecklingen inom den organisk-syntetiska storindustrin och dess återverkan på den nordiska industrin»

§ 3. Efter mötet höll prof. J. L. Simonsen på inbjudan av Delegationen för Finlands Kemister ett föredrag över ämnet »*Sesquiterpene Ketones*». Föredraget publiceras i Meddelandena.

Kemiska Sällskapet i Åbo — Turun Kemistiseura.

Berättelse
över

Kemiska Sällskapets i Åbo verksamhet under året 1947.

Kemiska Sällskapet i Åbo har under det gångna året sammanträtt till inalles 5 ordinarie möten, vilka samtliga hållits i Åbo Akademis aud. V. Mötena ha i regel varit besökta av ett 15-tal medlemmar.

Liksom tidigare ha kemiestuderande vid Akademien inbjudits bevista mötena. Enligt överenskommelse ha Turun Kemistikerhos medlemmar inbjudits till mötena, liksom Sällskapets medlemmar beretts tillfälle närvara vid sagda förenings möten. Tillsammans med denna förening har Sällskapet dessutom anordnat gemensamma föredragstillfällen med såväl utländska som finländska gäster som föredragshållare, bland dem tre nobelpristagare. Dessa föredragstillfällen ha varit mycket välbesökta. Följande föredrag ha därvid hållits:

Prof. Liese Meitner, Stockholm: »Ueber die verschiedenen Spaltungsmöglichkeiten des Urans bei Bestrahlung mit Neutronen.»

Prof. Hans v. Euler, Stockholm: »Om nukeleinsyrornas kemiska egenskaper och biologiska roll.»

Prof. A. I. Virtanen, Helsingfors: »Adaptivisesta enzymien muodostumisesta mikroorganismeilla.»

Doc. Nils Gralén, Göteborg: »Äro konstfiber bättre än naturliga fibrer?»

Vid Sällskapets ordinarie möten ha följande föredrag hållits:

Fil.lic. Paul W. Lange, Stockholm: »Moderna fysikaliskkemiska metoder i träforskningens tjänst.»

Fil.dr Bertil Nybergh, Helsingfors: »Den tekniska forskningen och högskolorna.»

Prof. Helge Aspelund: »Om folinsyra.»

Prof. Anders Ringbom: »Amperometriska titreringar.»

Dipl.ing. Waldemar Jensen: »Plastics.»

Förvaltningen har under det gågna året handhafts av följande medlemmar:

Prof. Per Ekwall, ordförande
Dipl.ing. Nils Lindén, viceordförande
Fil.mag. Runar Birck, sekreterare
Prof. Anders Ringbom, medlem
Prof. Helge Aspelund, medlem
Övriga funktionärer utom styrelsen ha varit:
Dipl.ing. Waldemar Jensen, kassör
Dipl.ing. Nils Lindén, klubbhövding
Dipl.ing. I. Kjellman, revisor
Dipl.ing. O. Jansson, revisor
Dipl.ing. K. B. Reims, suppleant.

Under året ha 5 nya medlemmar intagits. Två medlemmar ha avgått med döden. Medlemsantalet vid årets slut uppgår till 57. Av dessa äro 17 bosatta å annan ort.

Åbo, den 1 januari 1948.

R. Birck
sekreterare.

Kemiska Sällskapets i Åbo medlemmar den 1 jan. 1948.

Andersson Jul., apotekare	Köpmansgatan 4 A.
Aspelund, Helge, prof.	Fredsgatan 2.
Augustsson, Anne-Marie, fil.mag.,	Åbo Akademi
Backman, Allan, dipl.ing.,	Pargas Kalkbergs A.B.
Birck, Runar, fil.mag.,	Kyrkogatan 3.
Björkqvist, Karl, dipl.ing.,	Fredsgatan 23, Vasa.
Candelin, Max, dipl.ing.,	Pargas Kalkbergs A.B.
Casagrande, Wittorio, dipl.ing.,	Puolalagatan 4 A 11.
Doepel, Henning, dipl.ing.,	Pargas Kalkbergs A.B.
Ekwall, Per, prof.,	Åbo Akademi.
Forss, Bengt, dipl.ing.,	Åbo Akademi.
Geitlin, Bertel, fil.mag.,	Pargas Kalkbergs A.B.
Gustafsson, Olof, dipl.ing.,	Jalostaja O.Y.
Grönroos, Herbert, dipl.ing.,	Aningaisgatan 3.
Harva, Olavi, dipl.ing.,	Nylandsgatan 14.
Hasan, Abraham, dipl.ing.,	Lilla Tavastgatan 16.
Hausen, Hans, prof.,	Vårdbergsgatan 8.
Holmberg, Bror, prof.,	Stockholm.
Holmberg, Gustaf-Adolf, fil.mag.,	Slottsgatan 59 D.
Hofman, Erik, fil.mag.,	Martinsgatan 4.
Hultin, Sven Olof, dipl.ing.,	Nystad, Makeis ja Mehu Oy.
Jansson, Ossian, dipl.ing.,	Nylandsgatan 5 B.
Jensen, Waldemar, dipl.ing.,	Gezeliusgatan 2.
Kajander, Lisa, fil.mag.,	Tureborgsgatan 2.
Kivalo, Pekka, dipl.ing.,	Åbo Klädesfabrik.
Kjellman, Ingvald, dipl.ing.,	Köpmansgatan 10.
Klingstedt, F. W. prof.,	Äänekoski.
Lagerbohm, Max-Åke, fil.mag.,	Kaskisgatan 11 D.
Lindén, Nils, dipl.ing.,	Stålarmsgatan 27.
Lonka, Matti, dipl.ing.,	Tureborgsgatan 2.
Lühr, Håkan, dipl.ing.,	Tammer Tehtaat Oy, Tammerfors.
Metzger, Adolf, fil.dr.,	Pargas Kalkbergs A.B.
Nylund, Gunnar, dipl.ing.,	Brahegatan 9 A.
Pehrman, Gunnar, prof.,	V. Strandgatan 17.
Pettersson, Ragnar, dipl.ing.,	Eriksgatan 6.
Qvist, Walter, prof.,	Brahegatan 2.
Rajalin, Erik, dipl.ing.,	Vattenverket, Hallis.
Reims, Kurt B., dipl.ing.,	Åbo Klädesfabrik.
Reims, Ulla, fil.mag.,	Åbo Klädesfabrik.
Remmer, Eila, dipl.ing.,	Åbo Akademi.
Remmer, Fjalar, dipl.ing.,	Åbo Porslinsfabrik.
Ringbom, Anders, prof.,	Vårdbergsgatan 8.
Ringvall, Alve, dipl.ing.,	Åbo Tvål.
Sahlberg, Uno, dipl.ing.,	Aningaisgatan 3.
Sarlin, Emil, bergsråd,	Pargas.
Saxén, Arne, dipl.ing.,	Lasarettsgatan 8 B.
Schröder, Inga, med.lic.,	Vårdbergsgatan 1.
Stigell, Jarl, dipl.ing.,	St. Tavastgatan 26.
Svahnström, Karl-Erik, dipl.ing.,	Åbo Porslinsfabrik.
Söderblom, Arne, dipl.ing.,	Åbo Tvål.
Troupp, Angelique, fil.mag.,	Gertrudsgatan 3.
Tuderman, John, fil.mag.,	St. Tavastgatan 21—23.
Wirta, Elis, dipl.ing.,	Klockringaregatan 7.

Extra medlemmar:

Johans, Lars, dipl.ing.,	Littois.
Pasel, Evert, dipl.ing.,	Pargas.
Salin, Jarl, prof.,	Slottsgatan 36.
Sätis, Hilding, prof.,	Eriksgatan 26 B.

Möte — Kokous.
5. IV. 1948.

Protokoll fört vid Kemiska Sällskapets i Åbo möte den 5 april 1948. Förhandlingarna leddes av ordförande prof. Ringbom. Närvarande voro 15 medlemmar och 1 studerande.

§ 1. Protokollet från årsmötet 11. 12. 47 upplästes och justerades.

§ 2. Sekreteraren föredrog årsberättelsen för år 1947.

§ 3. Revisionsberättelsen upplästes. Nettobehållningen från år 1947 utgjorde 7.747: 50 mk.

§ 4. Den avgående styrelsen beviljades tacksam ansvarsfrihet.

§ 5. Professor Walter Qvist redogjorde för de förhandlingar, som ägt rum vid de tekniska högskolornas rektorskonferens i Helsingfors under tiden 8—11 maj 1947.

Såsom en första fråga dryftades den riktiga översättningen till engelska av de tekniska högskolornas namn. Någon enighet i frågan kunde ej uppnås, utan framgick det att man på endel håll föredrog benämningen »Technical University» resp. »University of Technology», medan Kungliga Tekniska Högskolan i Stockholm antagit benämningen »The Royal Institute of Technology, Stockholm», enär »University»-benämningen ansetts missvisande med hänsyn till språkbruket i USA.

En omfattande behandling ägnades frågan om de principer, som borde gälla vid intagning av nya studerande, därest en begränsning ej kan undvikas. Förfaringssättet synes vara rätt likartat vid alla högskolor, i det att hänsyn i första hand tages till de resultat, som uppnåtts i studentexamen, kompletterade med skolresultatet. De mest framstående inträdessökandena kunna i allmänhet vinna inträde utan särskilda förhör, medan de allra sämsta lämnas å sido. För den mellanliggande gruppen har man på många håll infört psykotekniska prov till stöd för gallringen och ha resultaten av denna metod hittills visat sig gynnsamma.

En ej obetydlig uppmärksamhet ägnades frågan om de sociala och ekonomiska studiernas betydelse för de blivande ingenjörerna. Med uppskattning av hithörande läroämnens vikt och betydelse

betonades dock faran av en alltför stor splittring i undervisningen, om större kursfordringar införas i dessa ämnen.

Vid konferensen dryftades även en mängd frågor av ekonomisk natur gällande bl.a. studieavgifter, löneförhållanden, representationsfrågor, möjligheterna till ökad assistent- och kanslisthjälp för underlättande av lärarnas forskningsverksamhet m.m. Uppmärksamhet ägnades även frågan om förenklade former för utgivande av doktorsavhandlingar, varom förslag väcktes från universitetshåll i Sverige, syftande till att man skulle kunna disputera för doktorsgrad med ett antal utgivna publikationer, kompletterade med en sammanfattande redogörelse jämte litteraturregister.

Det må ännu nämnas att redogörelse lämnades över studenternas bostadsförhållanden, varvid framgick att samma svårigheter möta vid så gott som varje högskola. Ansträngningar göras dock på alla håll för att finna en lösning på detta problem.

Rektorskonferensen i Helsingfors var den andra i ordningen efter kriget. Nästa konferens kommer att äga rum i Trondheim våren 1949.

§ 6. Föredragshållaren avtackades av ordföranden för den intressanta redogörelsen.

In fidem: *Eila Remmer.*

Sesquiterpene Ketones.*

By

J. L. Simonsen.

In considering a subject for my lecture to-day it seemed to me that probably the most suitable subject would be that dealing with my work on the chemistry of the sesquiterpene ketones since this opened up a new field in terpene chemistry and since much of the work was published during the war it may have been inaccessible to you. The subject has a further interest in that it points a moral and shows only too clearly the dangers which may befall us if we rely too readily on theory.

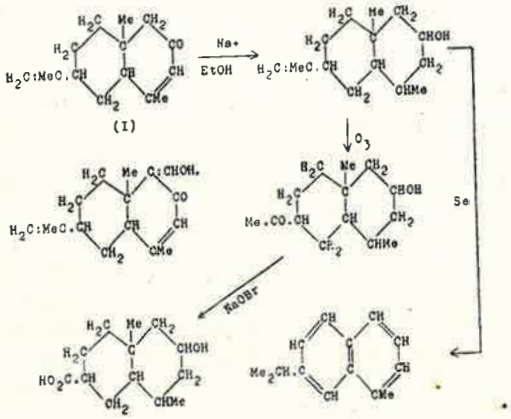
Although of course it has long been known that the majority of essential oils contain high boiling fractions, from which terpene hydrocarbons and alcohols had been isolated no naturally occurring ketones had been found to occur. In 1931 one of my colleagues in Australia, Mr. A. R. Penfold, drew my attention to a remarkable oil which he had separated from the wood of *Eremophila Mitchelli.* [1]) This was a viscid brown oil with an unusual and distinctive odour. On examination it was found to contain three crystalline ketones, eremophilone, $C_{15}H_{22}O$, hydroxyeremophilone, $C_{15}H_{22}O_2$, and hydroxydihydroeremophilone, $C_{15}H_{24}O_2$. I will not detain you with a description of the methods employed for their separation which afforded considerable difficulty which was not lessened by the fact that both eremophilone and hydroxyeremophilone were readily oxidised on exposure to the air. Our preliminary experiments showed that eremophilone was sesquiterpene ketone since it readily yielded a crystalline semicarbazone and it was therefore the first natural sesquiterpene ketone to be isolated. **

The elucidation of the structure of eremophilone did not at first appear to afford much difficulty. The ketone contained

* A lecture delivered before the Suomalaisten Kemistien Seura and Finska Kemistsamfundet in Helsingfors on April 12th 1948.

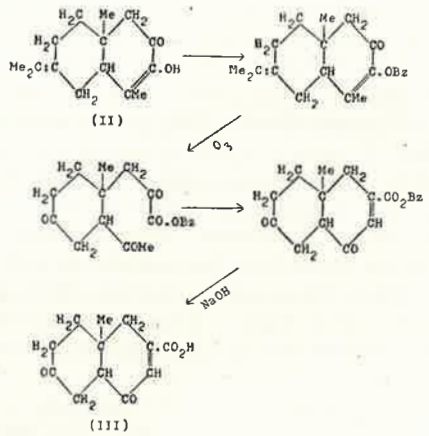
** It should be mentioned that Pfau and Plattner (Helv. Chim. Acta. 1934, 17, 729) at almost the same time separated from cedar wood oil two sesquiterpene ketones α- and β-atlantones.

two ethylenic linkages since it gave on catalytic hydrogenation tetrahydroeremophilone. One of these ethylenic linkages was in the α:β-position to the carbonyl group a fact readily proved (i) by its reduction with sodium and alcohol to dihydroeremophilol, (ii) by its oxidation with hydrogen peroxide to eremophilone oxide, a reaction shown by Weitz and Scheffer [2]) to be characteristic for ketones with an ethylenic linkage in the α:β-position to the carbonyl group and (iii) by its absorption spectrum. It contained also a $-CH_2$ group adjacent to the carbonyl group since it gave a hydroxymethylene derivative. The secondary alcohol, dihydroeremophilol gave on dehydrogenation with selenium the naphtalene hydrocarbon, eudalene, thus establishing the carbon skeleton. Furthermore since dihydroeremophilol gave on ozonolysis formaldehyde and a keto-alcohol it became clear that the second ethylenic linkage was present in an *iso*propenyl side chain. These simple reactions would appear to be accounted for by the scheme set out below: —



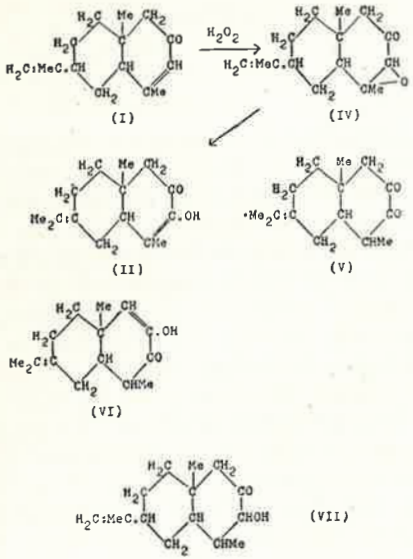
Whilst there are two other possible formulae for eremophilone with which I will not trouble you, a study of the chemistry of hydroxyeremophilone appeared to confirm structure (I) for the ketone. Hydroxyeremophilone showed somewhat remarkable properties. It behaved as a pseudo-phenol giving an intense blue-black colour with ferric chloride but, unlike diosphenol, it was insoluble in alkali. The presence of the hydroxy group was readily proved by the preparation of a highly crystalline benzoate but the carbonyl group was inert. When the benzoate was oxidised with ozone it gave acetone and a neutral product considered at the time to have the composition $C_{19}H_{18}O_5$. The formation of acetone indicated the presence of an *iso*propylidene side chain. On hydrolysis with alkali the neutral

product gave benzoic acid and a keto-acid thought to be $C_{12}H_{14}O_4$. These reactions seemed to occur in the manner shown by the formulae: —



I mentioned previously that when eremophilone was treated with hydrogen peroxide in alkaline solution an oxide was obtained. When this oxide was digested with acetic acid in the presence of sodium acetate and the product hydrolysed with alkali an oil was obtained which on benzoylation gave the benzoyl derivative of hydroxyeremophilone. This interesting reaction appeared to provide conclusive evidence that eremophilone must have structure (I) and the oxide (IV). Whilst these experiments appeared to show that hydroxyeremophilone was represented by (II) there was little doubt that it could also exist in the isomeric form (V) since although the crystalline solid was colourless it gave a bright yellow solution. The isomer (VI) is also possible. I need not trouble you with the evidence that dihydrohydroxy eremophilone had the formula (VII).

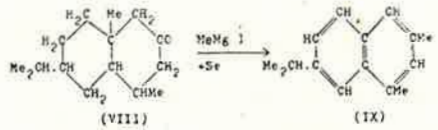
Before proceeding to consider further the structures of eremophilone and its cogeners there is one point of more general interest to which I would wish to direct your attention. You will have observed that whilst eremophilone contains an *iso*propenyl side chain hydroxyeremophilone contains an *iso*propylidene side chain. This type of isomerism is of course met with in the simpler terpenes such as geraniol, citronellal, citral and their crystalline derivatives and has been frequently discussed. It has been maintained that they are inseparable mixtures since they give on oxidation both acetone and formaldehyde. It has been suggested also that the formation of the aldehyde is due to an abnormal oxidation and they are all true *iso*propy-



lidene derivatives. It have always been against accepting the latter view since were it correct it would render doubtful any structure based upon oxidative degradation. Fortunately the development of infra-red spectroscopy has enabled this important question to be decided. Thompson and Whiffen [3] have proved conclusively that the simpler terpene derivatives, such as those referred to above are all of them mixtures of the two forms but that the percentages vary in different specimens. It is, as I feel sure you will all agree, gratifying that the direct chemical evidence should have been confirmed.

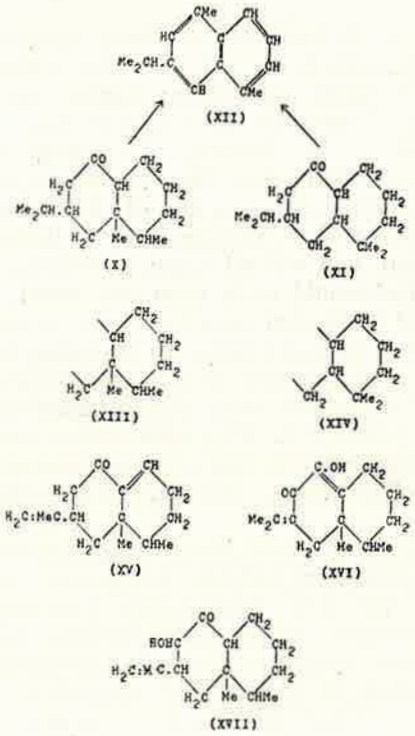
After this brief digression into theory let us return once more to the chemistry of eremophilone. In assigning its structure one assumption was made, namely that the methyl group eliminated when dihydroeremophilol was dehydrogenated to eudalene was situated in position 9. This assumption seemed justifiable on the basis of the isoprene rule and the extensive work of Ruzicka and his collaborators. We were now to find that it was incorrect.

In 1936 during the course of an investigation into the structure of another sesquiterpene ketone, *α*-cyperone, to which I will refer later, we required 1:3-dimethyl-7-*iso*propylnaphthalene (IX) and a convenient route to this hydrocarbon appeared to be by the selenium dehydrogenation of tetrahydroeremophilone (VIII) after treating it with methyl magnesium iodide. Much to our surprise we found that the hydrocarbon obtained in this



(VIII) (IX)

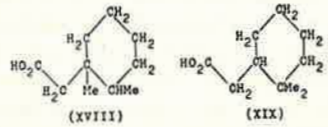
manner was 1:5-dimethyl-7-*iso*propylnaphthalene (XII). This proved of course that the carbonyl group in eremophilone could not be in the 3 position as had been assumed but in the 5. This necessitated a complete reconsideration of the evidence upon which the structure of the ketone had been based and it indicated further that the methyl group eliminated on dehydrogenation of dihydroeremophilol could not be in position 9. If it had occupied this position it was not possible to accommodate a $-CH_2$ group and an α:β-ethylenic linkage adjacent to the carbonyl group. It seemed therefore probable that tetrahydroeremophilone must be represented by either (X) or (XI) from either of which 1:5-dimethyl-7-*iso*propylnaphthalene (XII) could be prepared. It was anticipated that it might be possible to distinguish between (X) and (XI) by the degradation of eremophilone or one of its derivatives to substances containing the



(XII) (X) (XI) (XIII) (XIV) (XV) (XVI) (XVII)

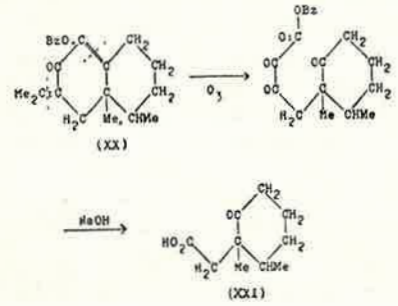
carbon skeletons represented by (XIII) or (XIV) which could be synthesised. I will not bore you with an account of the long series of experiments which were required before final proof was obtained that the following formulae correctly represented eremophilone, hydroxyeremophilone and dihydrohydroxyeremophilone.

As I have already mentioned it was observed that when hydroxyeremophilone benzoate was oxidised with ozone a neutral compound was obtained. This was at the time considered to have the formula $C_{19}H_{18}O_5$ and it was found on hydrolysis with alkali to give benzoic acid and a ketoacid, which, on the basis of the analysis of the semicarbazone, was given the formula $C_{12}H_{14}O_4$. A reinvestigation of these products showed that the neutral substance actually had the formula $C_{19}H_{20}O_5$ whilst the keto-acid had the composition $C_{10}H_{16}O_3$ and was found to have m.p. 105—107°. By the reduction of the keto-acid by the Clemmensen method an optically active liquid acid, $C_{10}H_{18}O_2$, characterised by the preparation of its crystalline *p*-phenylphenacyl ester, m.p. 65—67°, was prepared. This acid was a *cyclo*hexane derivative since it gave on dehydrogenation with selenium *o*-xylene. It can therefore be represented by either (XVIII) or (XIX). These two acids were synthesised and resolved into their optical enantiomorphs and the synthetic acid was found



(XVIII) (XIX)

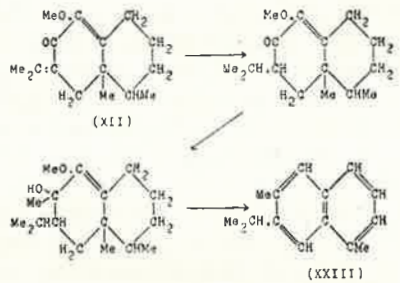
to be identical with (XVIII). The identification of this acid left no doubt that hydroxyeremophilone must be (XVI), the oxidation of its benzoate (XX) proceeding in accordance with the following scheme when the keto acid would be (XXI).



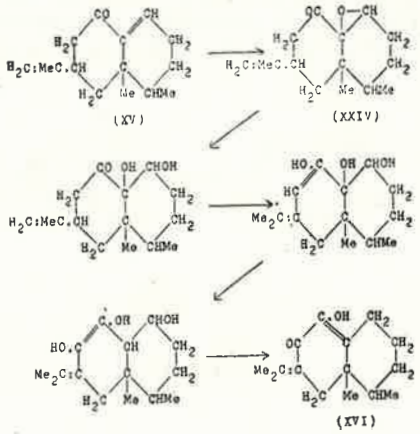
(XX) (XXI)

Confirmatory evidence in support of the carbonyl group being in position 6 was obtained by the preparation of the methyl ether of the hydroxy-ketone (XXII) since this substance after catalytic hydrogenation and treatment with methyl magnesium iodide gave on selenium dehydrogenation 1:6-dimethyl-7-*iso*-propylnaphthalene (XXIII).

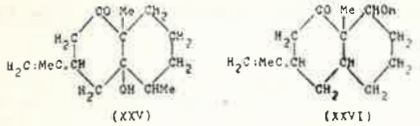
The structure of hydroxyeremophilone having thus been placed on an assured basis there can be no doubt that eremophilone and dihydrohydroxyeremophilone must be represented by the for-



mulae which I have already shown you. This structure for hydroxyeremophilone explains very simply why the *iso*propenyl side chain in eremophilone changes so readily into the *iso*propylidene side chain when the hydroxy-ketone is prepared from the oxide since there is naturally a tendency for the ethylenic linkages to conjugate. There remains however one somewhat difficult reaction to elucidate. With the new formula for eremophilone the oxide must be represented by (XXIV) and the mechanism of its conversion into hydroxyeremophilone is somewhat obscure. I would venture to suggest that it proceeds in accordance with the scheme: —



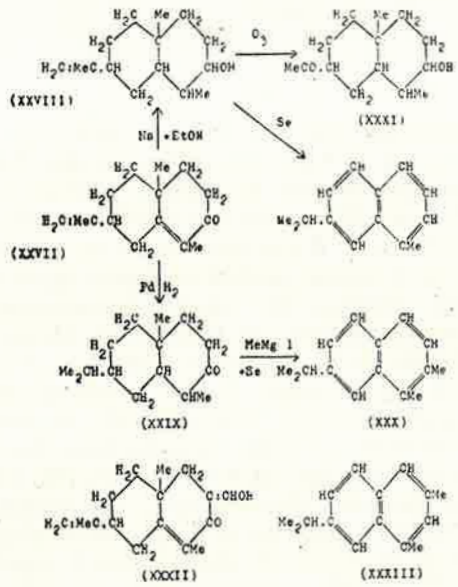
I have dealt in some detail with the chemistry of these ketones since so far as I am aware they provide the first instance in terpene chemistry in which the isoprene rule is broken. There is however a possible explanation for this. Is it not possible that in the plant the primary product is a keto-alcohol having either formula (XXV) or (XXVI)? This would pass into eremophilone by loss of water accompanied by a molecular rearrangement.



As is so frequently the case when a new type of naturally occurring substance is observed others rapidly follow. I have mentioned already the two atlantones studied by Pfau and Plattner which was followed by the brilliant work of the Swiss school on the vetivones. I was also myself fortunate in receiving at this time from a former Indian assistant another ketone, *α*-cyperone, which occurs in the oil of *Cuperus rotundus*.[4]) This is also a eudalene derivative and I shall now attempt to describe to you very briefly how its constitution was determined and how it has been synthesised. As the result of the experience which we had gained we had little difficulty in determining the structure of *α*-cyperone. Unlike eremophilone this ketone gives a number of crystalline derivatives of which the 2:4-dinitrophenylhydrazone is the most characteristic. The evidence on which the structure (XXVII) is based is (i) it is a eudalene derivative since on reduction with sodium and alcohol it yields dihydro-*α*-cyperol (XXVIII) which gives eudalene on dehydrogenation; (ii) the reduction with sodium and alcohol to the secondary alcohol suggest that one ethylenic linkage is in *α*:*β*-position to the carbonyl group which was confirmed by the absorption spectrum; (iii) the ketone contains two ethylenic linkages since on catalytic hydrogenation tetrahydro-*α*-cyperone (XXIX) is obtained; (iv) the carbonyl group is in position 2 since tetrahydro-*α*-cyperone gave after treatment with methyl magnesium iodide 1:2-dimethyl-7-*iso*propylnaphthalene (XXX) on dehydrogenation; (v) the second ethylenic linkage is situated in an *iso*propenyl side chain since the ozonolysis of dihydro-*α*-cyperol 2:5-dinitrobenzoate gave formaldehyde and a crystalline ketone (XXXI) giving iodoform with potassium hypoiodate; (vi) the ketone has a $-CH_2$ group adjacent to the carbonyl group since it yields a hydroxymethylene derivate (XXXII) yielding after

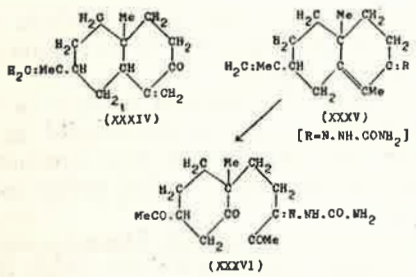
catalytic hydrogenation and dehydrogenation 1:3-dimethyl-7-*iso*propylnaphthalene (XXIII). Proof that α-cyperone could not have the alternative formula (XXXIV) was obtained by the ozonolysis of its semicarbazone (XXXV) when a crystalline semicarbazone (XXXVI), $C_{15}H_{23}O_4N_3$ was obtained. If the ethylenic linkage had been exocyclic the composition of this would have been $C_{14}H_{20}O_3N_3$.

Although α-cyperone can be distilled without decomposition under reduced pressure it is comparatively readily isomerised when warmed with alkalies or oxalic acid. The isomeric ketone,

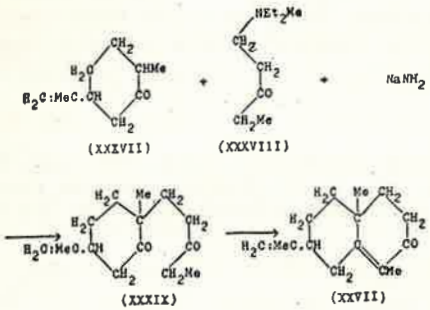


β-cyperone, is a stereoisomeride and not a structural isomeride since its semicarbazone gives on ozonolysis the same product as does that of α-cyperone. It must therefore be presumed that the two ketones differ only in the special arrangement of the methyl and *iso*propenyl groups.

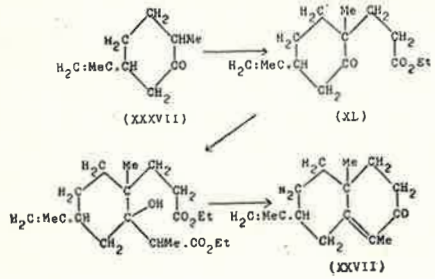
The structure assigned to the α- and β-cyperones has been confirmed by two independent syntheses carried out in Professor Sir Robert Robinson's and my laboratories. The first very elegant synthesis leads to both ketones. By the condensation of the methiodide of 1-diethylaminopentan-3-one (XXXVIII) with the sodio-derivative of *l*-dihydrocarvone (XXXVII) a crystalline diketone (XXXIX) was obtained. When this diketone was cyclised with sodium ethoxide in benzene solution it



gave a ketone which by the comparison of derivatives was clearly indentical with α-cyperone. If however concentrated sulphuric acid was used for the cyclisation β-cyperone was obtained.



The second synthesis followed more conventional lines. The sodio-derivative of 1-dihydrocarvone was condensed with ethyl β-chloropropionate to give the ester (XL). Condensation of this ester with ethyl α-bromopropionate in the presence of zinc gave a mixture of products which, after prolonged fractionation, gave as the main fraction an oil from which, on hydrolysis with alcoholic potassium hydroxide, a ketone was obtained yielding derivatives identical with those derived from β-cyperone. Further on reduction with sodium and alcohol a secondary alcohol



was prepared the 3:5-dinitrobenzoate of which did not on admixture depress the melting point of the same derivative prepared from dihydro-*a*-cyperol.

Whilst the synthesis of a natural product is always of interest I would suggest that the special interest in these two syntheses lies in that they provide the first synthetic proof of the position occupied by the angle methyl group in sesquiterpenes derived from eudalene.

I have in this lecture attempted, I fear, to cover a somewhat wide field but I trust that it may encourage some of you to re-examine the high boiling fractions of essential oils. It may be argued that investigations of this type are of little value being in the main merely an experimental and intellectual amusement. From this view I would wish to dissociate myself. Only when we know the structure of all plant products and understand the part which they play in the plant metabolism can we hope to place the greatest human industry, agriculture, on a truly scientific basis. I can conceive no finer object.

References.

[1]) *Bradfield, Penfold* and *Simonsen*, J.C.S., 1932, 2744; J. Proc. Roy, Soc. New South Wales, 1933, 66, 420; *Bradfield, Hellström, Penfold* and *Simonsen*, J.C.S. 1938, 767; *Adamson, Marlov* and *Simonsen*, ibid., 774; *Penfold* and *Simonsen*, ibid., 1939, 87; *Copp* and *Simonsen*, ibid. 1940, 415; *Gillam, Lynas-Gray, Penfold* and *Simonsen* ibid. 1941; 415.

[2]) Ber., 1921, **54**, 2327.

[3]) J.C.S. in the press.

[4]) *Bradfield, Hegde, Rao, Simonsen* and *Gillam*, J.S.S. 1936, 667; *Bradfield, Pritchard* and *Simonsen*, ibid. 1937, 760; *Adamson, McQullin, Robinson* and *Simonsen*, ibid. 1576.

Lubricating Oil from Pine Tar and Tall Oil.

2nd Report: The Effect of Catalysts on the Decarboxylation of Resin Acids from Tall Oil and Tall Oil Pitch [1]).

By *Terje Enkvist* and *Keijo Mäkelä*.

Experiments by Thord Bröderman, Björn Erik Sjöblom and Runar Svensson.

Report from the A. B. Centrallaboratorium and the Chemical Departments of the University and of the Institute of Technology, Helsingfors.

1. The Purpose of the Investigation.

The present report describes investigations carried out in connection with the research undertaken to develop methods of manufacturing lubricating oil from pine tar and tall oil, and performed on the initiative of Dr. Bertil Nybergh at the A. B. Centrallaboratorium during the years 1940—1945. The 1st Report[1]) on this work contained an investigation of the composition of the most important raw material, the oven pine stump tar, used during the war for the production of lubricating oil in Finland. The tar samples employed in the investigation were supplied by the plant at Maavesi. This tar contained only about 30 % of matter which may be called lubricating oil, present already in the original tar*. Furthermore the tar contained about 16 % of free resin acids which resembled those of tall oil. When heated these acids decomposed to viscous, high-boiling hydrocarbons and could be used to increase the yield of lubricating oil.

The reaction of decomposing resin acids to yield hydrocarbons has been used for a long time in the manufacture of rosin oil by heating rosin and, probably to some extent, it takes place also in the manufacture of pine tar from pine wood or stumps.

* A separate distillation (not described in Report 1) of the neutral matter of the tar from Maavesi gave oil with B. P. 170—240° at 10 mm in a yield of 29,7 % calculated on the original tar.

According to earlier studies[2]) the main reactions involved are (1) and (2):

(1) $C_{19}H_{29} \cdot CO_2H = C_{19}H_{30} + CO_2$
Rosin acid — Abietene

(2) $C_{19}H_{29} \cdot CO_2H = C_{19}H_{28} + CO + H_2O$
Rosin acid — Abietine

In practice, however, these simple decarboxylations always are complicated by other reactions. Already before decarboxylation the abietic acid-type acids of rosin are isomerized from levopimaric over proabietic to abietic acid[3]), and the abietic acid ($C_{19}H_{29} \cdot CO_2H$) is then disproportionated to the so called pyroabietic acid[4]), which is chiefly composed of a mixture of dehydroabietic ($C_{19}H_{27} \cdot CO_2H$), dihydroabietic ($C_{19}H_{31} \cdot CO_2H$), and tetrahydroabietic ($C_{19}H_{33} \cdot CO_2H$) acids. Both of the hydrocarbons »abietene» and »abietine» resulting from tha decarboxylations are, according to *Lombard*[5]), mixtures of isomers, and can easily be disproportionated to »pyroabietene» and »pyroabietine», which are mixtures of hydrogenated and dehydrogenated abietenes or abietines. Decomposition during which methane developes may also occur after or perhaps before[2]) decarboxylation, yielding various hydroretenes[5]) and, when combined with dehydrogenation, even the crystalline hydrocarbon retene $C_{18}H_{18}$ itself[6]), for example according to reaction (3):

(3) $C_{19}H_{28} = C_{18}H_{18} + CH_4 + 6\,H$
Abietine — Retene

Analyses of the gas mixtures evolved (table 13) show that generally the ratio between the volume of hydrogen and that of methane is lower than the ratio 3 : 1 predicted by the reaction (3). The corresponding observation was made by *Vesterberg* when heating abietic acid or rosin together with nickel on pumice[7]). Obviously the hydrogen of the reaction (3) is, to a great part, absorbed by hydrogenation of other components of the reaction mixture or by other reactions. (Vesterberg speaks of »intern oxydation» during which carbon monoxide and water develop).

Further decomposition resulting in the rupture of rings, transposition and removal of side chains, condensation and polymerization is possible also[5]). Even the formation of rosin acid anhydrides $(C_{19}H_{29} \cdot CO)_2O$ and of ketones $(C_{19}H_{29})_2CO$ has been discussed[8]), but it does not seem probable. Another reaction worth attention, and found by one of us to be possible in the formation of pitch on distilling tall oil[9]), is the one in which the

carboxyl group of one resin acid molecule associates with an ethylene bond of another thus forming a slowly saponifiable acid ester (4):

(4) $C_{19}H_{29} \cdot CO_2H + C_{19}H_{29} \cdot CO_2H = C_{19}H_{29} \cdot CO_2 \cdot C_{19}H_{30} \cdot CO_2H$

In the manufacture of lubricating oil from material containing resin acid, first of all a decarboxylation as complete as possible is of importance. Second, the formation of retene or other crystalline matter must be avoided. Third, the hydrocarbons obtained should, contrarily to rosin oil for painting purposes, be as non-drying as possible, that is, they should show low iodine numbers and contain as much saturated groups or benzene nuclei and as little unsaturated aliphatic or alicyclic bonds as possible.

The decarboxylation of resin acids of pine tar can be effected simply by heating, for instance by distilling the tar at ordinary pressure or even at elevated[10]) pressure. Distillations of pine tar employing ordinary pressure, a temperature range of about 350—400° C in the tar, and no catalysts nor steam were carried out by one of us together with the late Chemical Engineer *Pentti Asikainen* at Centrallaboratorium in 1940—1941, but showed, however, that the resulting heavy oils with boiling points of about 300—360°C often have comparatively low viscosities, and sometimes, especially when stored in a cold place, solidify precipitating crystalline matter. The same was experienced in Sweden also on technical use of lubricating oil manufactured by simple distillation of pine tar and there, for the purpose of obtaining better results in some cases, as reported by *Frey* in 1944[11]), the distillation was carried out at a somewhat lowered temperature by conducting the gases evolved through the tar. Already in 1941 we found that the above described drawbacks could be eliminated by decarboxylation at a lower temperature, namely at about 300°C, followed by distillation with superheated steam. In doing this it proved useful and even necessary to speed up the main reaction, i.e. the decarboxylation, by using catalysts which gave the main reaction the required preference over the interfering side reaction, i.e. the demethylation-dehydrogenation to retene. The use of catalysts in the decarboxylation of the acids is of still more importance in the manufacture of lubricating oil from tall oil and tall oil pitch, as these materials contain a greater amount of acids and far less unsaponifiable matter than pine tar.

For long it has been known that catalysts accelerate the decarboxylation of resin acids. In the literature the following catalysts are mentioned: kaoline, pumice, coke[12]), activated carbon [13]) [14]). bleaching earth[15]), fullerite, Wilkinite, silicagel,

silica, $CaSO_4$, norite, copper chromite, alumina[14]), lime, baryte[15]), $CaCO_3$ [13])[16]), CaO, $Ca(OH)_2$, $CaCl_2$, Ca-formiate, Ca-acetate[17]), V_2O_5, ZnO, Cr_2O_3, MnO, CuO, MoO_3, Co or oxides or hydroxides thereof, Zn-dust[19]), Al dust[20]), Pt[14]), silicic, boric[18]) and phosphoric acid, salts of phosphoric acid [18])[21])[22]), silicotungstic acid[17]) benzene-, toluene- and naphtalene sulfonic acids [23]), $ZnCl_2$ [24])[25])[22]), $SnCl_2$, CuCl[25]), $AlCl_3$ [26]), and oxalates of Ni, Fe, Co and Mn[27]). Especially the catalysts $AlCl_3$, $ZnCl_2$, $FeCl_3$ [28]) and Fe_2O_3 are specifically mentioned in connection with pine tar. However, at the time we began our work in 1941, many of the investigations listed above were not yet published, and very little was known about the true effectivity and behaviour of the catalysts at different temperatures. It was soon found that many of the above named »catalysts» were practically inactive at 300° C. This led us to undertake an extensive study of the catalytical decarboxylation of pure resin acids as well as that of pine tar, tall oil, and tall oil pitch. A preliminary report on the first experiments with abietic acid was published by one of us early in 1942 [30]).

Our experiments comprise both comparatively simple orientating test tube experiments with pure resin acids, tall oil, and tall oil pitch in the presence of various catalysts, and complete laboratory cooks of lubricating oil from pine tar, tall oil and tall oil pitch. Since especially tall oil also contains large amounts of fatty acids, the test tube experiments were carried out also with samples of fatty acids, a preliminary report on this having been published at the beginning of 1944[31]). The present report principally concerns the test tube experiments carried out with resin acids, while the complete cooks and the test tube experiments with fatty acids will be described in later reports.

Experiments concerning catalytical decarboxylation of resin acids are of interest not only to the manufacture of lubricating oil from pine tar and tall oil, but also to the production of rosin oil from rosin and, in an opposite sense, to the industry of distillation of tall oil. In the latter industry it is of essential importance to avoid decarboxylation of the resin and fatty acids, and to know whether the metals used in the apparata and the impurities of the crude tall oil possibly catalyze the decomposition of the acids of tall oil to hydrocarbons and other unsaponifiable matter, which debase the distilled oil.

2. Survey of the Experimental Procedures Used.

In most of the test tube experiments — type 1 — weighed amounts of usually 0,5 or 1,5 g of the various substrates — resin acid, tall oil or tall oil pitch — were heated with weighed amounts of the catalysts for certain periods of time in open or loosely

stoppered test tubes held in a salt bath of constant temperature, usually 300 ± 2°C. In some of the experiments a current of dried, air-free carbon dioxide was led over the surface of the substance in the test tube. In certain cases the reaction mixture was stirred occasionally with a glass rod. The heating was sometimes performed in a steam-bath containing boiling benzophenone (B. P. 306°).

In the more detailed experiments — type 2 — the substances were held in test tubes sealed with rubber stoppers. The gases developed were led, by means of a current of pure carbon dioxide, through concentrated potassium hydroxide solution into a gas buret, where the volume of the undissolved gases (CO, H_2, CH_4 and other gaseous hydrocarbons) was determined. The water developed and the volatile oils formed were absorbed in a tube containing calcium chloride[32]).

In the most detailed experiments — type 3 — 0,050 moles of the resin acid in the presence of a suitable catalyst were heated in rubber-stoppered suction tubes placed in a salt bath. The temperature both in the salt bath and in the reaction mixture was measured with a thermometer immersed therein and occasionally the reaction mixture was stirred by a glass rod with gas tight bearing fixed in the stopper. The gases evolved were collected over salt solution in a gas buret, the water and the volatile oil formed being absorbed in a tube containing calcium chloride. After the experiment the collected gas was analyzed by means of an Orsath-apparatus[8]).

In all of the experiments the acid and in many cases also the saponification and iodine (Hübl-Waller, 18 hours) numbers, of the reaction mixture were determined after the heating. In the experiments of type 3 even the decrease in weight of the reaction mixture was determined and the reaction mixture in most cases divided, mainly according to the saponification and extraction method with petroleum ether recommended by Spitz and Hönig[33]), into unsaponifiable matter and undecarboxylated acids.

In the following the results of the experiments are presented mostly in the form of tables.

The concentrations of the catalysts are reported partly as percentages of the substrate used — i.e. resin acid, respectively tall oil or pitch of tall oil —, partly as the ratio C : A, where C is the number of g-equivalents of catalyst and A the number of g-equivalents of resin acids, respectively total acids in tall oil or in pitch of tall oil. The ratio C : A was calculated according to the formula (5):

(5) $C : A = 561\ p/se$, where s is the acid number (mg KOH/g) of the used substrate (resin acid, tall oil or pitch of tall oil), p the concentration of catalyst as per cent of the substrate and

e the equivalent weight of the catalyst. The number 561 equals 10 KOH. For e the common equivalent weights were mostly used, for example Fe/2, $Ni(OCOCH_3)_2 \cdot 4H_2O/2$, $FeCl_3/3$, $Fe(OCO \cdot C_{19}H_{29})_3/3$ and so on.

For most catalysts also the net decrease (d) in the acid number caused by the decarboxylation reaction is reported in the tables. Thereby the decrease in acid number caused by the neutralization and dilution through the addition of catalyst was deduced from the total observed decrease in acid number. The neutralization effect of the catalyst was calculated — somewhat schematically — assuming that the metals and bases employed neutralize an equivalent amount of resin acid. In case of salts of volatile acids, such as chlorides, nitrates and acetates, it was assumed (see pages 38 and 39), that the neutralization reactions ran according to the equations (6) and (7):

(6) $FeCl_2 + C_{19}H_{29} \cdot CO_2H = C_{19}H_{29} \cdot CO_2 \cdot FeCl + HCl$
(7) $FeCl_3 + 2C_{19}H_{29} \cdot CO_2H = (C_{19}H_{29}CO_2)_2 \cdot FeCl + 2\ HCl.$

Thus for example each of the molecules $ZnCl_2$, $FeCl_2$, $MnCl_2$, $NiCl_2$ or nickel acetate neutralize one molecule of resin acid, whereas each molecule of either ferric chloride or ferric nitrate neutralizes two molecules of resin acid.

The total decrease ($\triangle$) in acid number caused by the catalyst through neutralization and dilution was calculated from the formula (8):

$$(8)\quad \triangle = p(s/100 + 561/fe) = \frac{s}{100}\left(p + \frac{100}{f} \cdot \frac{C}{A}\right)$$

In this formula the factor f usually is equal to 1. If salts of bivalent metals with volatile acids are used as catalysts, f is equal to 2, and for salts of trivalent metals with volatile acids f is equal to $1\ ^1/_2$.

The net decrease in acid number by decarboxylation (d) was calculated by deducing $\triangle$ from the difference between the acid number (s) of the substrate and the acid number of the reaction mixture determined after the experiment. Thus the effect of the decrease in weight during the experiment did not be observed in the calculations.

In many cases also the catalytic activity (AV) of the catalyst as defined by Langenbeck [34]) (equivalents of substrate decomposed in 5 minutes by each equivalent of catalyst) was calculated, the decrease in acid number caused in the corresponging experiment without catalyst being subtracted from the net decrease in acid number caused by decarboxylation (d) in the experiment with catalyst. The formula (9) was used:

$$(9)\quad AV = \frac{(d—b)}{1000\ C/A} \cdot \frac{27}{m}$$

Therein b denotes the decrease in acid number in the corresponding experiment without catalyst and m the time of heating in minutes.

3. The Various Substrates.

a. The Crystalline Resin Acides.

Only some years ago the crystalline resin acid of tall oil was considered chiefly to consist of only one chemical compound, called »pinabietic acid»[35]) by O. Aschan. This acid, however, proved [36]) to be mainly a mixture of abietic acid and the components of the »pyroabietic acid» (see p. 22). Obviously, when »pinabietic acid» is used for decarboxylation experiments, the variegated composition thereof is a detriment. On the other hand, the isolation of sufficient quantities of truly pure chemical inviduals from the tall oil resin acid mixture is a very tedious process[37]). Abietic acid can be isolated somewhat more readily from gum rosin, but during the war we did not dispose of this raw material in the quantities required. Furthermore »pinabietic acid» resembles the actual mixture of resin acids in tall oil and even in pine tar more than pure abietic acid. As some kg:s of »pinabetic acid», purified by the co-workers of O. Aschan and stored in glass bottles sealed by melting the necks of the bottles, were at our disposal, we used this material as it was after recrystallization, and checked the results by analyzing the used »pinabietic acid» and by carrying out some catalytical decarboxylations with samples of abietic and dehydroabietic acid and also of resin acids from pine tar.

The melting point (M. P.) of the »pinabietic acid» used as starting materials was 168—170°. It was recrystallized from hot methanol or ethanol and dried in vacuo over calcium chloride in a desiccator previously filled with carbon dioxide.

2,00 g of »pinabietic acid» of the batch 5, table 3, M. P. 171—174 and $[\alpha]_D + 3{,}2°$ (2,8 g in 100 ml of 99% ethanol) gave, when treated according to the method of Hasselström [36]) and dried at 100° C, 0,91 g of dehydroabietic acid sulfonate, which corresponds to a 36 per cent content of dehydroabietic acid in the »pinabietic acid». This content is markedly higher than those found in the experiments run by Hasselström, who when working with crude pinabietic acid, obtained the maximum value of 18 per cent of dehydroabietic acid as sulfonate. Presumably this difference is caused by the accumulation of the dehydroabietic acid in the »pinabietic acid» during recrystallization. —

20 g of the batch 6, (table 5) of the »pinabietic acid», M. P. 170—173° and iodine N:o g J/100 g gave 7,5 g of the sulfonate and only 0,2 g of hydroxytetrahydroabietic lactone with M. P. 129—130°. 2,5 g of the thus obtained sulfonate gave when further treated [36]), 1,4 g dimethyl ester of dehydroabietic acid sulfonate with M. P. 177—178°.

A b i e t i c a c i d (crude). This acid was obtained by distillation of American gum rosin at a pressure of 8 mm, and recrystallization of the distillate from ethanol. M. P. 152°, acid No 167 mg KOH/9. It was stored in a vessel filled with carbon dioxide.

D e h y d r o a b i e t i c a c i d (crude). It was obtained by dehydrogenation of abietic acid with sulfur according to Lombard[38]), and recrystallization from ethanol. M. P. 126°, acid No 149 mg KOH/g.

Furthermore, in some experiments (table 17), crystalline r e s i n a c i d s f r o m p i n e t a r (acid No 179, $[\alpha]_D^{15}$ + 30,8°), and also a corresponding sample of petrol-ether-insoluble »o x y r e s i n a c i d s» from pine tar (acid No 158) were used. Both samples are described in the 1 st Report.[1])

b. The Crude Tall Oil and the Tall Oil Pitch.

In tall oil and tall oil pitch the resin acids mingle with fatty acids and insaponifiable substances and also with such recognized catalyst poisons as compounds of bivalent sulfur. Our investigations of the catalytical decarboxylation of fatty acids later to be reported show, that on the whole, the same catalysts accelerate the decarboxylation of both fatty and resin acids, but that for attaining the same velocity of decarboxylation the fatty acids under conditions otherwise similar require a temperature approximately 30° higher than that used for resin acids. In decarboxylation experiments with tall oil and tall oil pitch under conditions so mild that only a limited part of the material decomposes, substantially the resin acids should be decarboxylated (see p. 33).

Moreover, test tube decarboxylation experiments with crude tall oil and tall oil pitch in the presence of various catalysts were carried out. The compositions of the samples employed are presented in the tables 8—10.

Also with pine tar some test tube catalytic decarbocylations were performed. As pine tar after the distilling off of the volatile components thereof has a composition much more complicated and a acid number substantially lower than those of resin acids or tall oil, the test tube experiments with pine tar do not give results as clear as those with resin acids and tall oil wherefore they are not given in the present report. The most of our catalytic experiments with pine tar were carried out as more or less complete cooks of lubricating oil and will be described in later reports.

4. The Effect of the Nature and Purity of the Substrate and of Variations in the Experimental Procedure.

A comparison between experiments performed with and without a current of carbon dioxide (compare in table 1 exp. No 1 with No 10, exp. 2—5 and 7 with 6,8,9 and 11; exp. 38, table 2, with 51, table 4; 90, table 6, with 122, table 7; 163, table 10, with 201, table 11) showed that the decreases in acid number did not differ very much. As a rule the decreases in acid numbers were 10—20 per cent greater in the experiments carried out in presence of air than otherwise. This difference, presumably, is due to oxidation of the resin acid, the oxygen of air promoting formation of alcoholic hydroxyl groups, which subsequently are esterified with the carboxyls.

Use of test tubes made of different kinds of glass, and also variations in the purification (boiling with water, steaming) of test tubes had virtually no effect on the decrease in the acid number (table 1). On the other hand, impurities in the resin acid were found to have marked effects. A small quantity of an alcohol-insoluble, inorganic impurity, which proved to have a very marked catalytic decarboxylating effect on being heated together with the pure resin acid, was isolated from the used tall oil resin acid sample itself (exp. Nr 12—16, table 1). The smallness of the quantity of this impurity allowed no quantitative analysis, but a qualitative spectroscopical analysis carried out by mag. Åke Renwall revealed the precence of i.a. calcium, aluminium, titan and silicium. No bleaching earth had been used in purifying the resin acid.

Samples of »pinabietic acid» from the various batches of crystallization showed no appreciable differences in velocity of decarboxylation. Dilution of the »pinabietic acid» with neutral lubricating oil from pine tar (table 1, exp. 21—23) had no special or unexpected effect on the decarboxylation velocity.

The samples of »pinabietic acid», used for the experiments were chiefly mixtures of the components of »pyroabietic acid» (p. 22). It seems possible that some of the resin acids of this mixture decompose faster than the others. After an experiment, in which only a part of the resin acids decomposes, it would be of interest to know whether the remaining acids on being isolated and subjected to a new decarboxylation experiment would decompose slower than the original resin acid mixture. To investigate this question some decarboxylation tests were made with the resin

acids (separated from the unsaponifiables as described on p. 25), which had remained as acids in a test run for partial decarboxylation of the »pinabietic acid» in the presence of an iron powder catalyst. In addition to this experiments were made with — somewhat crude — samples of abietic and dehydroabietic acid (No 92—94 and 100—102, see also note 1, table 6). The results seem to indicate that dehydroabietic acid and especially the resin acids remaining from a former decarboxylation experiment decarboxylate in the presence of an iron or a ferrous chloride catalyst appreciably slower than the original resin acid mixture (»pinabietic acid») and even slower than abietic acid. Experiments with resin acids isolated from pine tar (table 17) show that these even seem to decarboxylate slower than resin acids from tall oil.

The impurities of crude tall oil seem to impair considerably, although not totally, the effect of such catalysts as nickel acetate and also phosphoric acid, sulfuric acid and especially phosphotungstic acid, whereas iron bearing catalysts are effective in crude tall oil even(compare tables 2—6 witch table 8).

Tall oil pitch may have various compositions. Even the different samples of pitch used in our experiments, and supplied by the Enso-Gutzeit tall oil distillation plant of Kotka varied considerably depending on how far the distillation had advanced. Two series of experiments were made with two different samples of tall oil pitch. The analytical data pertaining to sample 1 are given in table 10. The sample 2 showed acid No 71, saponification No 85, content of unsaponifiables 14,9 %, of resin acids 35,9 % and of fatty and other readily esterifiable acids 47,9 %. Obviously the sample 1 originated from a distillation, which had been interrupted at a stage earlier than that from which sample 2 came. When these samples were heated in test tubes in the presence of catalysts markedly different results were obtained. On the other hand the decarboxylation of the not so strongly condensed and polymerized pitch No 1 obviously was accelerated by many catalysts, which had no appreciable effect on the more heated, condensed and polymerized pitch No 2. Even in the sample No 1 the catalytical activity was markedly weaker than in experiments with crystalline resin acids. This behaviour can be explained by the hypothesis concerning formation of pitch of tall oil described on page 22 (reaction 4) [9]). A strong heating of tall oil causes the resin acid molecules to become attached to each other and to the fatty acids, the carboxyl of the resin acid being bound during the formation of slowly saponifiable acid esters. Such strongly heated pitch as that in sample 2 will then contain only small amounts of free resin acid carboxyl and can not be greatly affected by catalysts at a temperature of about 300° C.

Crude tall oil and also pitch of tall oil contain sulfur and therefore develop hydrogen sulfide when heated. Sulfur compounds and especially hydrogen sulfide are well known poisons to many catalysts, especially nickel compounds. In some experiments the sulfur compounds were removed, at least partially, by heating pitch of tall oil — in some cases after the addition of chlorinated lime, lead acetate or mercury oxide — to 300°, 310° or 325° C, and passing a stream of carbon dioxide or superheated steam through the pitch until the evolution of hydrogen sulfide ceased. Subsequently, the thus pretreated pitch was heated in the presence of the catalysts. Even for such catalysts as nickel nitrate or -acetate an improvement of the decarboxylation effect could not be observed with certainty. The corresponding pretreatment of crude tall oil did not improve the effect of nickel acetate and to a certain extent decreased the effect of toluene sulphonic acid and of m-sulfanilic acid.

5. Acceleration of the Decarboxylation by Various Unmixed Catalysts.

a. Effect of Bleaching Earth and of Sodium Hydroxide.

A sample of bleaching earth was found to have a strong catalytic effect on the decarboxylation of resin acid from tall oil (exp. 17, table 1). The catalyst did not dissolve in the resin acid. On the other hand, a small amount of sodium hydroxide was found to have a retarding effect on the decarboxylation (compare exp. 18 with the experiments 6, 8, 9 and 11, table 1).

b. Iron and Nickel Compounds. Compounds of Other Metals.

Many substances acknowledged as catalysts for other reactions proved to have no or almost no effect on the decarboxylation reaction, at least under the experimental conditions employed (temperature about 300° C). Such was the case with i.a. $Bi(NO_3)_3$, CuCl, $Th(NO_3)_4 \cdot 4H_2O$, As-compounds (table 2), $PtCl_4$, $AgNO_3$, $HgNO_3$ (table 3), V_2O_5 (table 4), $SnCl_4$, (table 5), copper compounds, NH_4VO_3, J, $KHSO_4$ (table 11 with additions, p. 35) and most Al-compounds (table 2 and p. 35).

The references to tables mentioned hereinabove and hereinafter also refer to the footnotes which follow some tables and present experiments wherein the catalytic effect was slight or lacking.

Iron- and nickel compounds showed an evident although a moderate catalytic effect, the activity values AV varying up to 1,64 (exp. 123, table 7) and 6,15 (exp. 299, table 17) respectively. Great differences of activity were found between different salts

of the same metals. As to nickel and iron compounds the chlorides and nitrates, especially of iron (tables 2—4, 6—11, 13 and 17), and, in the case of nickel, even the acetate ($Ni(OCOCH_3)_2 \cdot 4H_2O$) (tables 2, 3, 8, 9, 11, 13, 17 and 18) were particularly active. Decarboxylation experiments carried out under identical conditions gave with most catalysts very nearly coincident results (see e. g. table 18, note about exp. 320—326). In the experiments with nickel acetate,hower, great variations in activity even in experiments carried out in a current of CO_2 were observed, although the concentrations were maintained constant (compare exp. 52 and 320, table 18). These experiments were made with different samples of nickel acetate and resin acid and by different workers. It is a well known fact that the activity of nickel catalysts, e.g. for hydrogenation, can vary greatly depending on small differences in purity and manner of preparation. — Iron resinates were almost inactive (tables 2 and 6), but nickel resinate was, at least in one experiment (No 34, table 2), found distinctly active.

The nickel compounds and the iron compounds differ in that the nickel compounds, nitrates and acetates even, after a short time form a precipitate mainly containing metallic nickel (note 27, table 13), while the iron compounds give no such precipitate, but clear, pale solutions, which only at the end of the catalysis turn brown principally on the surface of the reaction mixture, obviously through the influence of the oxygen in air.

Nickel and iron carbonate and also the free metals showed less activity than chlorides and nitrates (tables 2—4, 6—9, 11, 13 and 17). Even metallic nickel on clay, obtained by heating nickel nitrate and subsequently reduced with hydrogen, did not catalyze decarboxylation, although nickel of the kind described is a well known hydrogenation catalyst. Iron oxide was almost inactive (table 3), nickel oxide showed some activity (table 2). Hydroxides, sulfates, formiates and phosphates of nickel and iron were mostly totally inactive under the experimental conditions employed (tables 3, 5, 7 and 11). The oxalate of nickel we found to be inactive in crystalline resin acid (table 5), the oxalate of iron in tall oil pitch likewise (table 10). *F. W. Klingstedt* [27]) found nickel- and iron oxalates to be active catalysts. The difference in temperature may be the cause of this contradictory fact, our experiments being made at 303° ± 2° resp. 310 ± 2°, whereas K. used 300—340°, with variations of 15—40° in each single experiment.

Both ferrous and ferric chlorides are active. No greater difference in activity seems to exist between iron chlorides containing various amounts of crystal water ($FeCl_2$, $FeCl_2 \cdot 4\,H_2O$, $FeCl_3$, $FeCl_3 \cdot H_2O$, $FeCl_3 \cdot 6H_2O$, tables 2, 6—11 and 17).

The concentrations of nickel and iron salts required to affect substantially the velocity of decarboxylation are rather high, namely for iron and iron compounds about 0,25—1,0 % Fe of the amount of the resin acids, for nickel compounds (as % Ni) somewhat less. At such comparatively high concentrations as these not only the catalytical decarboxylation effect, but also the neutralization effect of metals, metal oxides and salts of metals with volatile acids is appreciable.

As a rule the activity values of nickel compounds and of other catalysts investigated in this respect rise with sinking concentration (exp. 35 and 36, table 2; 50 and 51, 55 and 56, 58—60, table 4; 97 and 98, 105—107, table 6; 247—252, table 15). This is easy to explain. Obviously at higher concentrations the molecules of the catalysts are more associated to one another or otherwise disturb the effect of another more than at lower concentrations.

As to salts of metals other than nickel and iron the chlorides of zinc and of manganese were very active, other compounds of these metals being almost totally inactive (tables 2, 5 and 11). Calcium chloride showed some catalytic effects (tables 5 and 10). Cobalt and also copper compounds mostly caused no or almost no catalytic decrease in the acid numbers of the resin acids (tables 2, 3, 5 and 11). Cerium and zirconium dioxide (table 5) catalyzed the decarboxylation appreciably.

At a temperature of 300° and lower catalysts effective in tall oil should (p. 28) principally decarboxylate the resin acids, leaving the fatty acids relatively unchanged. From the values of resin acid numbers according to the experiment presented in the tables 8, 9 and 16 it is seen that this is true in the case of ferrous chloride, zinc chloride, nickel acetate and phosphotungstic acid. The selective decarboxylation of the resin acids is particularly pronounced in distilled tall oil (exp. 157—160, table 9), whereas it is not so marked in crude tall oil. On heating in the absence of catalysts or in the presence of slow working ones such as iron dust or calcium carbonate the resin and fatty acids seem to decarboxylate with approximately the same velocity.

c. *Tungstic, Phosphoric and Phosphotungstic Acid.*

The acid oxides of the elements of the group VI b of the periodic system are interesting catalysts. Chromic acid (CrO_3) seems to be inactive (table 2), molybdic acid (MoO_3) has only a slight effect (table 4), but tungstic acid (WO_3) is a strong catalyst with great activity especially in small concentrations (tables 4 and 18). Uranic acid (UO_3) is active also (table 5), but less so than tungstic acid. Uranyl nitrate showed no catalytic effect worth mentioning (table 2).

Phosphoric acid and also phosphor pentoxide are acknowledged and fairly active decarboxylation catalysts (tables 2 and 8). By combining the catalytic power of phosphoric acid with that of tungstic acid a very strong catalyst is obtained. Indeed, phosphotungstic acid ($H_2PO_4 \cdot 12\ WO_3 \cdot 7\ H_2O$) is, as far as we know, the strongest decarboxylation catalyst for crystalline resin acids, only 0,02 % of it bringing about very marked effects (tables 4, 5, 9, 13 and 17). Unfortunately, its catalytic effect seems to be rather strongly poisoned by the impurities of crude tall oil and of tall oil pitch (tables 8, 9 and 10). — In the tables the phosphotungstic acid is designated with P-W-acid, and as its equivalent weight the value 125,1 = 1/24 of the molecular weight was applied.

Phosphotungstic acid has been used before as a catalyst for the structural rearrangement of terpenes [39]) and also as a color reagent for resin acids [40]) but, as far as we know, not as a catalyst for decarboxylation.

Ammonium tungstate and sodium phosphate were inactive or almost inactive (tables 4 and 2). The effects of the phosphoric, tungstic and phosphotungstic acids seem to be due to the acid and complex forming functions of these substances.

d. Sulfuric Acid and Organic Sulfonic Acids.

Another group of acid catalysts comprises sulfuric acid and a variety of organic sulfonic acids. Sulfuric acid seems to be a catalyst not much less active than phosphoric acid (table 2). About equally active is chlorsulfonic acid (table 5). The nitric and hydrochloric acids have no appreciable decarboxylation effect (tables 3 and 10). This might be due to their volatility under the used experimental conditions.

It is known that sulfuric acid reacts readily with dehydroabietic acid forming a sulfonic acid, the dehydroabietic acid sulfonate $C_{19}H_{26}(SO_3H)CO_2H$ [36]). We found that the catalytic effect of this sulfonic acid is of the same order as the effect of sulfuric acid itself (table 4). Possibly the effect of sulfuric acid is due to the formation of this sulfonation product.

The p-toluenesulfonic acid and further more cymene sulfonic acid, naphtol yellow S (free 2,4-dinitronaphtol-(1)-sulfonic acid) (7) and camphorsulfonic acid (table 12) are catalytically highly active. Contrarily to naphtol yellow S some other naphtolsulfonic acids, namely 1,4-,1,5- and 2,6- naphtolsulfonic acids and the 1, 4, 8- and 1, 3, 8-naphtol-disulfonic acids were found to be totally or almost totally inactive. The three isomeric anilinsulfonic acids behave in an interesting way as the o- and p-isomers were totally inactive, whereas

the m-isomer (methanilic acid) is highly active (table 12). Also amidophenol-4-sulfonic acid was inactive.

The catalytic effect of m-sulfanilic acid (AV 4,77) is by far stronger than the effect of the equivalent amount of sulfuric acid (AV 0,42) or even dehydroabietic acid sulfonate (AV 1,80).

Additions to table 11. The following materials showed low catalytic effects: $Co(NO_3)_2$, $UO_2(NO_3)_2 \cdot 6\ H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$ and silicous earth »Dicalite»; no or almost no effect: Ni-dust, $Ni(OH)_2$, Ni-formiate, $NiSO_4$, $Ni_3(PO_4)_2$, ZnO, Zn-acetate, $AlCl_3$, $SnCl_2 \cdot 2\ H_2O$, $Cr(OH)_3$, MnO_2, NH_4VO_3, J, and $KHSO_4$. A mixture of Dicalite and nickel acetate gave a lower effect than Dicalite alone.

Experiment 180 b. Original pitch of tall oil was heated with 0,63% of its weight of $Ni(NO_3)_2$ at a temperature of about 300° without current of CO_2. The acid No was after 39 min. 85 mg KOH/g, after 90 min. 75, after further 30 min. heating and subsequent addition of further 0,63% by weight of $Ni(NO_3)_2$ and heating with it 110 min. 33 mg KOH/g, and after further 48 min. 27 mg KOH/g.

The combination $Ni(OH)_2$ —$Cu(OH)_2$ and $Ni(NO_3)_2$ —$CuSO_4$ were found to give roundly the same results as heating with $Ni(OH)_2$ respectively $Ni(NO_3)_2$ without admixture of copper compounds. The combination $Ni(NO_3)_2$ (0,63%) and Cu-acetate (0,14%) very nearly gave the same result as $Ni(NO_3)_2$ —$CuCO_3$ in exp. 189.

6. Differences in the Course of the Decarboxylation Caused by the Various Catalysts.

Some experiments with greater amounts of resin acids (type 3, table 13) revealed marked differences between the effects of some of the most important catalysts. The results of the analyses of the gas mixture developed during the experiments were particularly characteristic.

It is known through the work of La Lande [8]) that two main decarboxylation reactions (1) and (2) (p. 22) exist and that the reaction (1) in absence of catalysts dominates at lower temperatures, until about 330° C, and reaction (2) at higher temperatures. Our two decarboxylation experiments (226 and 227 in table 13) without catalysts at 350° and about 380° are in close agreement with the results of La Lande and show that the formation of carbon monoxide dominates at these high temperatures, especially at about 380°, the proportion $CO : CO_2$ (by volume) being 2,35 and 5,70—8,26 (at various stages) respectively. Even methane and hydrogen are developed in considerable amounts,

although the sum of the quantities of these gases is only from a sixth to a tenth part of the sum of the amounts of the carbon oxides. The proportion $H_2 : CH_4$ was 0,69 respectively 0,47—0,69, thus much smaller than what the equation (3) would require, if all hydrogen were to be developed as hydrogen gas. Iron powder and also ferrous resinate at about 300° give much carbon dioxide, much less carbon monoxide and considerable quantities of hydrogen. It seems as if ferrous resinate has a special power to develop methane. Ferrous chloride at 280° and 300° and also ferric chloride at 300° give roundly about equal amounts of carbon monoxide and carbon dioxide ($CO : CO_2$ 0,96—1,19 in the experiments 231, 232, 234 and 235, and 1,55 in the exp. 233), only very little hydrogen and not much methane. Nickel acetate at 302° and 306° and also at 350° gives much carbon oxide, much less carbon dioxide ($CO : CO_2$ 4,5—6,9 and 3,21 respectively) and hydrogen in about the same quantities as iron powder. Nickel acetate also gives some methane, especially during the later stages of the reaction, but anyway much less than nickel on pumice according to Vesterberg [7]). Finally phosphotungstic acid at 302° gives much carbon monoxide, much less carbon dioxide ($CO : CO_2$ 2,3) almost no hydrogen and very little methane.

Table 13 presents the acid numbers of the reaction mixtures found by titration and also the corresponding acid numbers summarily calculated from the amounts of the developed carbon oxides according to the reactions (1) and (2) (p. 22). In the calculation the effect of neutralization and dilution by the catalysts and also the effect of the decrease in weight of the reaction mixtures were observed. In the cases where this decrease had not been determined by weighing, it was assumed to be 10 % of the weight of the reaction mixture. In most cases the values of acid numbers found by titration agree well with those obtained by calculation. However, in the experiments without catalyst or with iron powder as catalyst a somewhat greater decrease in acid number is found than that calculatable from the amount of the carbon oxides developed. Reactions such as the formation of resin acid anhydrides or acid esters thus can not be observed in the experiments with phosphotungstic acid, nickel acetate or iron chlorides as catalysts, but they are possible in the experiments without catalyst or with iron powder as catalyst.

The neutral matter obtained with some of the catalysts was isolated, distilled in vacuo and analyzed. The results (table 14) show, that the distillates consist mainly of hydrocarbons. The analyses revealed abietine ($C_{19}H_{28}$) when nickel acetate had been used as catalyst in the experiments, but a mixture of abietine and abietene ($C_{19}H_{30}$) when ferrous chloride or phosphotungstic acid had been used as catalysts. This answers expectations: according to the reactions (1) and (2) (p. 22) such a catalyst as nickel acetate which gives mainly carbon monoxide should also yield abietine, and catalysts such as ferrous chloride, and phosphotungstic acid, which give both carbon dioxide and carbon monoxide in considerable quantities, should yield a mixture of abietene and abietine. Quantities of oxygen containing substances (ketones and so on) worth mentioning were not found in the neutral distillates.

A striking feature is that the remaining not decarboxylated acids in all of the investigated cases show a very low iodine number, whereas the iodine number of the neutral matter and also that of the original resin acid before heating are much higher. Even in the values of the rotation power a great difference is found between the original resin acid mixture, the »pinabietic acid» having $[\alpha]_D$ about 0°, and the not decarboxylated resin acid mixture left after heating with catalyst having $(\alpha)_D$ about + 50°. These facts suggest that the bulk of the resin acids after heating consists of dehydroabietic acid, which possesses a benzene nucleus and in pure state shows the iodine No 0 and $[\alpha]_D$ + 62°. As described on p. 30 both dehydroabietic acid and the resin acids left after heating decarboxylate when heated with iron or ferrous chloride considerably slower than the original »pinabietic acid».

7. The Effect of Time and Temperature. Development of Hydrogen Chloride by Metal Chloride Catalysts.

Experiments at various temperatures were made principally with ferrous chloride and with zinc chloride as catalysts. Zinc chloride begins to show its effect in resin acid already at about 170° (table 15) and in crude tall oil at some temperature between 206 and 266° (table 16) The increase in the effect with rising temperature is moderate, in any event much slower than that which can be calculated from the known rule of van't Hoff, according to which a 10° rise of temperature roundly doubles the reaction velocity. Furthermore the effect of zinc chloride, especially at the lower temperatures, is rather slow after the first half an hour of heating. Ferrous chloride is a weaker catalyst than zinc chloride. It catalyzes appreciably at 280° and its effect seems to increase comparatively rapidly when the temperature rises to 300, 310 and 320° (tables 6, 10 and 13), approximately obeying the rule of van't Hoff. Its effect also seems to decrease less rapidly than the effect of zinc chloride after the first half an hour (see development of gas in the exp. 233, table 13).

The table 13 shows that ferrous and ferric chloride, nickel acetate and phosphotungstic acid in moderate concentrations

cause roundly the same or even greater development of gas at 300° than heating in the absence of a catalyst at 350° C. At 350° the rapidity with which the decarboxylation with nickel acetate proceeds is manifold as compared to that at 300°, the decarboxylation at 350° being almost complete in about an hour's time.

We found the iron chlorides under the used experimental conditions develop much hydrogen chloride, e.g. in the exp. Nr 304, table 17 nearly 2/3 of the amount theoretically possible according to the reaction (8).

$$(8)\ FeCl_3 + 3C_{19}H_{29} \cdot CO_2H = Fe(C_{19}H_{29} \cdot CO_2)_3 + 3HCl$$

Naturally the equilibrium of such a reaction at room temperature lies almost totally to the left, but at about 300° C the hydrogen chloride is very volatile causing the reaction to shift to the right.

It may be assumed that the differences between the effects of iron chlorides and of zinc chloride lie therein, that the zinc chloride acts principally as a complex-forming, acidic catalyst[43]), whose effect rapidly decreases as the acidic catalyst decomposes during development of hydrogen chloride. In the iron chlorides, on the other hand, the principal catalyst may be supposed to be the iron ion, which is not destroyed by the development of the hydrogen chloride. The fact that the iron chlorides are more active than the iron resinates an probably be attributed to the greater dissociation of the chlorides than of the resinates, wherefore the former give more iron ions than the latter. True, the iron chlorides during the heating process are converted into resinates, but a part of the chloride ion remains in the reaction mixture, the conversion thus being incomplete.

The development of hydrogen chloride from the iron chloride catalysts can naturally, if not prevented, cause considerable corrosion of the iron of the apparatus unit on using these catalysts in the lubricating oil plants. For this reason it was found desirable to investigate means for diminishing this corrosion without decreasing the catalytic effect of iron chloride. On the suggestion of Engineer Hj. Ström of the lubricating oil plant of O. Y. Kanter A. B. at Seinäjoki (Östermyra) experiments in which ferric chloride was preheated in a separate vessel with various heavy oils prior to its use as catalyst were made. In the experiments carried out with pine tar good results were obtained by heating neutral lubricating oil from pine tar with its own weight of crystalline ferric chloride for 2 hours at 170° C. In doing this about 2/3 of the chloride was found in the distillate as hydrogen chloride. As the thus pretreated catalyst was used for decarboxylation of pine tar at 300° C it showed almost the same effect as the original iron chloride, and only

about 1% of the chlorine of the original ferric chloride was split off as hydrogen chloride. A corresponding test tube experiment in which ferric chloride was pretreated for 1 hour at 170° C with its own weight of neutral oil obtained by catalytic decarboxylation of pure resin acids (from exp. 234, table 13) with ferric chloride developed only about a third of the chlorine as hydrogen chloride (table 13, note 7). The following decarboxylation of pure resin acids (exp. 235, table 13) showed the pretreated catalyst to be almost as effective as the original ferric chloride. Presumably the ferric chloride in the pretreatment forms some kind of a mixed iron compound according to the equations (8) or (9):

$$(8)\ FeCl_3 + ROH = ROFeCl_2 + HCl$$
$$(9)\ FeCl_3 + 2\,ROH = (RO)_2\,FeCl + 2\,HCl$$

The R may be an organic radical such as an acidyl group of a resin acid, or perhaps an alkyl from a wax alcohol of the pine tar lubricating oil, as this does not consist of pure hydrocarbons, but contains ordinarily about 4% of oxygen. Obviously the resulting mixed chlorides have retained the catalytic properties of the ferric chloride. Only about one molecule of hydrogen chloride is split off for each iron atom on heating ferric chloride with neutral oil obtained from decarboxylation of pure resin acids whereas two molecules of hydrogen chloride are developed on heating ferric chloride with pine tar lubricating oil. Presumably this can be explained by the fact that the former oil contains less organic hydroxyl groups than the latter.

8. Use of Catalysts Together with Basic Substances.

Another conceivable way of decreasing the corrosion caused by acidic catalysts is the addition of basic reagents to the reaction mixture. Before contemplating the application of such a measure as this it is, of course, necessary to ascertain whether the addition of bases does not impair the effect of the catalysts too much. Experiments with samples of crystalline resin acids (table 17) showed that the addition of a small amount of lime (1,4% $Ca(OH)_2$) does not at all impair the effect of phosphotungstic acid, but that it seems to have a certain, although not a very great deleterious effect on the decarboxylation by iron powder, ferric chloride and nickel acetate. In this connection it may be mentioned, that in laboratory cooks of lubricating oil from pine tar the addition of 1,4% of lime did no harm, but that in the corresponding cooks from crude tall oil a very marked deleterious effect of the lime was observed on using iron powder or ferric chloride as catalysts, especially when the reaction was driven to almost complete decarboxylation of the organic acids.

In test tube experiments on using ferrous chloride as catalyst in tall oil pitch (table 10) it was observed that calcium hydroxide and calcium carbonate show a considerable impairing effect, ammonia in water solution and ammonium carbonate a smaller impairing effect, whereas sodium carbonate and sodium acetate totally destroy the catalytic effect. Furthermore it was found that the ammonia and the ammonium carbonate are practically speaking totally volatile under the experimental conditions (300° C). Consequently, it should be possible to diminish the corrosion of the unit apparatus caused by hydrogen chloride developed from iron chloride catalysts by adding ammonia or ammonium carbonate to the reaction mixture. The ammonia will then appear in the distillate obtained from the reaction mixture during decarboxylation, partly as ammonium chloride, and can be recovered and reused in a subsequent batch.

The use of a limited quantity of lime in the reaction mixture may be important and even advantageous othervise than for prevention of corrosion caused by hydrogen chloride or acetic acid. In the catalytic manufacture of lubricating oil the pine tar or crude tall oil are first heated with catalysts for 1—6 hours at about 300° C. The bulk of the resin and fatty acids are then decarboxylated, but always considerable quantities of these acids remain. If basic reagents were not used, in the subsequent distillation with superheated steam the acids would follow the lubricating oil into the distillate and thus would cause difficulties by forming emulsions when washing the distillates with lye. On adding some lime to the reaction mixture prior to the distillation the distillates will contain such little amounts of acids (acid numbers smaller than 10 mg KOH/g) as not to cause difficulties in the subsequent washing with lye.

9. Activation of Nickel Catalysts by Alanine and Betaine.

There was no advantage in the use of the mixtures of several substances as catalysts in most of the investigated instances. Such was the case with the mixtures tungstic acid—nickel acetate (table 18), $Ni(NO_3)_2$ — $CuCO_3$, $Ni(NO_3)_2$ — Cu-dust, $Ni(NO_3)_2$ — Fe-dust, $NiCO_3$ — $CuCO_3$, $Ni(NO_3)_2$, — $Cu(NO_3)_2$, $Ni(NO_3)_2$ — $CuSO_4$, nickel acetate—bleaching earth (Dicalite) (table 11) $FeCl_2$ — Zn-dust, and $FeCl_2$ — ZnO (table 10). Only the use of the admixture of sorbite and especially of dl-alanine or betaine with nickel acetate markedly promoted the catalytic effects (table 18). The amino acids and the sorbite mentioned were totally inactive if used alone, but had the power of improving substantially the effect of nickel acetate (formation of nickel complexes?). Salicylic acid and pyrocatechine did not show any such improving effect on nickel acetate (table 18).

Summary.

I.a. the following observations were made on heating resin acids from tall oil or pine tar and also samples of crude and distilled tall oil and tall oil pitch with decarboxylation catalysts at about 300—310°:

Bleaching earth and also an inorganic impurity found in the used samples of resin acids from tall oil have a strong decarboxylating effect, although they do not dissolve in the reaction mixture. Sodium hydroxide seems to be an inhibitor for the decarboxylation of resin acids (heading 5 a).

Chlorides and nitrates of iron and nickel as also nickel acetate are active catalysts, but the amounts required are rather large, roundly 0,20—1,0 % calculated as Ni or Fe. Iron resinates are almost inactive, nickel resinate can be an active catalyst. Carbonates of nickel and iron are somewhat active, whereas nickel and iron dust are very feeble catalysts. Hydroxides, sulfates, formiates, phosphates and oxalates of nickel and iron were found almost totally inactive at the used experimental conditions (heading 5 b). Catalytically active nickel and iron salts dissolve in the resin acid mixture during heating. After a short time nickel salts form precipitates of metallic nickel, whereas iron salts do not give corresponding precipitates. Iron chlorides develop approximately equal amounts of carbon dioxide and carbon monoxide and yield mixtures of abietene and abietine as high boiling reaction products. Nickel acetate gives principally carbon monoxide and abietine, and also considerable quantities of hydrogen and methane (heading 6).

Alanine and betaine, although without effect when used alone, activate the effect of nickel acetate (heading 9).

The chlorides of zinc and manganese, and also to some degree calcium chloride, are active catalysts (heading 5 b). Zinc chloride is effective from about 170° upwards, iron chlorides from about 280°. The metal chloride catalysts develop hydrogen chloride during the decarboxylation. Ferric chloride can be heated before use with roundly its own weight of lubricating oil from pine tar at 170° without impairing the effect of the catalyst. Thereby the hydrogen chloride is split off principally already during the pretreatment and thus does not corrode the equipment during the decarboxylation proper (heading 7).

Addition of calcium hydroxide or -carbonate impair appreciably but not totally the effect of ferric chloride and nickel acetate in resin acids from tall oil. Addition of sodium carbonate or -acetate destroys the effect of ferrous chloride in tall oil pitch, whereas ammonia and ammonium carbonate show only slight impairing effects (heading 8).

Cerium and zirconium dioxide catalyze the decarboxylation of resin acids from tall oil (heading 5 b).

Sulfuric acid and, even more, some organic sulfonic acids are effective catalysts. Such are the p-toluene- and cymene-sulfonic acids, naphtol yellow S and aniline sulfonic acid, whereas i.a. the o- and p-anilinesulfonic acids are totally inactive (heading 5d).

Tungstic and especially phosphotungstic acid are very active catalysts. The latter gives at 302° mostly abietine and carbon monoxide, furthermore some carbon dioxide, but almost no hydrogen nor methane. The phosphotungstic acid is effective even at concentrations of about 0.02%, but it is strongly poisoned by the impurities of tall oil and tall oil pitch (headings 5 b and 6).

After partial decarboxylation of the resin acids of tall oil the remaining resin acids seem to consist principally of dehydroabietic acid, which, at least with iron or iron chloride catalysts, decarboxylates slower than the original mixture of resin acids from tall oil. Even resin acids isolated from pine tar seem to decarboxylate somewhat slower than the resin acids from tall oil (heading 4).

The effect of nickel acetate, phosphoric and sulfuric acid is considerably less in crude tall oil and in tall oil pitch than in isolated resin acids from tall oil, whereas iron bearing catalysts are effective in crude tall oil even. In tall oil pitch the effect of iron bearing catalysts generally is weaker than in isolated resin acids from tall oil and practically amounts to nothing if the distillation of tall oil, at which the pitch is obtained, has progressed very far (headings 4 and 5 b).

In tall oil, especially in distilled tall oil, the decarboxylation catalysts at 300° decompose chiefly the resin acids, leaving the fatty acids to a great part undecarboxylated (heading 5 b).

Table 1. *Experiments with Various Samples of Resin Acid from Tall Oil. Effect of i. a. Bleaching Earth, Lye and Dilution with Neutral Oil.*

Temperature 300° C.

Exp. No	Resin acid batch No	Test tubes: Glass	Test tubes: Treatment	Catalyst	Special conditions	With (+) or without (—) CO_2	Time min.	mg KOH/g: Acid No	mg KOH/g: Saponification No
1	1 [1]	Common	Boiling 2 h. in water	—	—	—	30	157	171
2	1 [1]	»	—»—	—	—	—	140	116	118
3	2	»	—»—	—	—	—	140	102	105
4	2	»	Boiling and washing with alcohol	—	—	—	140	108	111
5	2	»	Steaming	—	—	—	140	118	131
6	2	»	Boiling 2 h. in water	—	—	+	140	137	150
7	2	Pyrex	—»—	—	—	—	140	119	121
8	2	»	—»—	—	—	+	140	125	127
9	2	»	Steaming	—	—	+	140	139	151
10	3 [2]	»	»	—	—	+	30	151	154
11	3 [2]	»	»	—	—	+	140	127	141
12	2	New, common	Boiling 2 h. in water	Catalyst undissolved			140	93	94
13	2	» »	—»—	Inorg. impurity 0,2 %		—	140	58	68
14	2	Pyrex	Steaming	» » 1, 4 »		+	140	81	83
15	2	»	»	» » 0,15 »		+	140	36	39
16	2	»	»	» » 0, 3 »		+	140	4	11
17	3 [2]	»	»	» » 1, 5 »		+	140	14	14
18	3 [2]	»	»	Bleaching earth 0,2 NaOH, 0,12 %		+	140	150	156
19	1 [1]	Common	Boiling 2 h. in water	Fe, 0,11 »		—	30	157	160
20	1 [1]	»	—»—	Fe, 0,11 »		—	140	88	94
21	1 [1]	»	—»—	—	Neutral oil, 3,61 parts [3]	—	30	34	42
22	1 [1]	»	—»—	Fe, 0,11 %	Same, 3,71 p. [4]	—	30	37	43
23	1 [1]	»	—»—	Fe, 0,11 »	» 3,58 p. [5]	—	140	26	41

[1]) M. P. 172—176°. — [2]) Recrystallized twice. — [3]) Diluted with lubricating oil from pine tar, 3,61 parts on each part of resin acid. — [4]) 3,71 parts of the lubricating oil for each part at resin acid. — [5]) 3,58. parts of lubricating oil.

Table 2. *Some Unmixed Catalysts in Purified Resin Acid from Tall Oil, without Current of CO_2.*

Temperature 306,5° C. Time of heating 30 min. M. P. of resin acid (batch 4) 177°, acid No 185, saponificat. No 187, iodine No 94, amount 1,5112 g = 0,005 moles.

Exp. No	Catalyst			Characteristic No:s after exp.			Decrease in acid No through decarboxyl.	Activity value of catalyst (p. 26)
	Kind	Concentration		mg KOH/g		Iodine No (Hübl-Waller) g J/100 g		
		%	C:A	Acid No	Saponfiic No			
24	—	—	—	179	—	77	6	—
25	$AlCl_3$	2,94	0,20	157	163	86	—3	0
26	H_3PO_4	2,29	0,21	100	107	79	108[1])	0,44
27	P_2O_5	2,01	0,26	47	58	83	170[2])	0,57
28	H_2SO_4	3,67	0,23	107	118	74	114	0,42
29	$CoCO_3.6\,H_2O$	7,50	0,20	77	142	66	57	0,23
30	$CoCO_3.\,6\,H_2O$	1,50	0,04	156	169	81	19	0,29
31	Fe	1,85	0,20	130	155	68	14	0,04
32	Fe-resinate[3])	21,8	0,20	131	152	65	12	0,03
33	$FeCl_3\,.\,6\,H_2O$	5,97	0,20	77	84	61	72	0,30
34	Ni-resinate[4])	5,0	0,04	116	122	85	60	1,21
35	NiO	2,47	0,20	85	97	86	58	0,23
36	NiO	0,50	0,04	151	156	79	26	0,45
37	Ni-acetate[5])	8,21	0,20	90	98	76	61	0,25
38	$NiCl_2$	0,86	0,04	122	129	57	57	1,14

The following materials were without or almost without catalytic effect: $CaCO_3$, $Zn(NO_3)_2 \cdot 6\,H_2O$, ZnO, $Bi(NO_3)_3 \cdot 5\,H_2O$, CrO_3, $UO_2(NO_2)_2 \cdot 6\,H_2O$, $MnB_4O_7 \cdot 5\,H_2O$, $MnCO_3$, $Mn(OCOCH_3)_2 \cdot 4\,H_2O$, MnO_2, CuCl, $Al(OH)_3$, Al_2O_3, $Th(NO_3)_4 \cdot 4\,H_2O$, $Na_2HPO_4 \cdot 12\,H_2O$, As_2O_3, As_2O_5, Ni on a clay carrier, obtained by igniting dust of porous clay impregnated with nickel acetate solution and reduced in hydrogen at 360° C.

[1]) Assuming that only 2/3 of the acid reacts during titration.

[2]) Assuming that only 2/3 of the formed phosphoric reacts during titration. [3]) Prepared by neutralizing an alcoholic solution of »pinabietic acid» with NaOH (indicator: phenolphtaleine) and precipitating with a solution of $FeSO_4$. Contained 8.32% Fe. — [4]) Prepared in manner similar to the preparation of the ferroresinate, precipitated with nickel acetate solution.

Table 3. *Some Unmixed Catalysts in Purified Resin Acid from Tall Oil, in current of CO_2.*

Experiment of type 2 (p. 25). Time of heating 30 min. Resin acid (batch 5) M. P. 171—174° acid no 185, $[\alpha]_D$ + 3,2°, amount 0,500 g.

Exp. No	Catalyst			Temperature °C	Acid No after exp.[4]) mg KOH/g	Gas, ml		Decrease in acid No, by decarb:n	Activity value of catalyst (p. 26) AV
	Kind	Concentration				insoluble in KOH	CO[1])		
		%	C:A						
39	—	—	—	301	161	0,72		24	
40	Co_3O_4	2,40	0,24	301	129	5,50	3,30	7	0
41	$NiCO_3$	1,18	0,06	306	110	14,14	11,31	61	0,56
42	$NiCl_2$	1,30	0,06	306	105	14,52	12,04	71	0,71
43	$Ni(NO_3)_2$	1,82	0,06	306	56	28,55	23,87	120	1,44
44	$Ni(NO_3)_2$	0,18	0,006	306		5,90	4,52		
45	$Ni(NO_3)_2$	[2])		306	121	5,60		63	1,12
46	Ni-acetate	0,24	0,006	306		5,70			
47	»	[3])		306	115	5,14	3,58	69	1,58

The following materials were without or almost without catalytic effect: Fe_2O_3, $Fe(OH)_3$, $AgNO_3$, $HgNO_3$, HNO_3, $PtCl_4$, $KMnO_4$.

[1]) Gas soluble in absorption liquor for CO ($CuCl—NH_3—NH_4Cl$). — [2]) Exp. no 44 continuted 30 min longer. — [3]) Exp. 46 continued 30 min longer. — [4]) The whole reaction mixture was titrated and the acid No calculated on the assumption that the remaining substance weighed 0,500 g.

Table 4. *Other Unmixed Catalysts in Purified Resin Acid from Tall Oil in Current of CO_2.*

Experiments of type 2 (p. 21). Time of heating 30 min. except in exp. 61. Resin acid of batch 4 (table 2), amount 1.511 g = 0.005 moles.

Exp. No	Catalyst: Kind	Catalyst: Concentration %	Catalyst: Concentration C : A	Temperature °C	After experiment: mg KOH/g: Acid No	After experiment: mg KOH/g: Saponificat No	After experiment: Iodine No	Gas, insoluble in KOH, ml	Decrease in acid No by decarb.:n	Activity value of catalyst
48	$FeCO_3$ [3])	0,89[5])	0,04	310	158	174	84	2,1	18	0,27
49	$NiCO_3$ [4])	0,73	0,031	311	155	163	69	23,5	23	0,49
50	$NiCl_2$	1,72	0,08	303	137	157	58	26,7	37	0,35
51	$NiCl_2$	0,86	0,04	305	135	143	60	26,8	44	0,85
52	Ni-acetate	1,65	0,04	310	149	156	74	28,0	29	0,52
53	$ZnCl_2$ [4])	0,90	0,04	303	110	118	82	21,6	69	1,42
54	Mo O_3	0,95	0,04	309	166	188	83	2,6	25	0,43
55	$WO_3 . H_2O$	1,66	0,04	304	15	24	86	177	174	3,69
56	$WO_3 . H_2O$	0,17	0,004	308	118	127	99	68	67	13,7
57	$(NH_4)_2WO_4$	9,40	0,20	310	109	116	82	25,3	58	0,32
58	P-W-acid	1,67	0,04	310	5	11	53	108	184	3,91
59	»	0,17	0,004	309	19	26	79	87,4	166	36,0
60	»	0,017	0,0004	311	125	134	91	27,8	60	135
61	$C_{19}H_{26}(SO_3H)CO_2H$	9,10[1])	0,072	311	92	110	70	35,4[2])	103	0,64
62	»	2,64	0,021	311	134	144	79	12,3	54	2,29

V_2O_5 was almost inactive.

[1]) In this experiment the time of heating was 60 min. — [2]) During the first 30 min. of heating 25,1 ml. — [3]) Made by precipitating ferrosulfate solution with sodium carbonate. Contained 41,7% Fe. — [4]) Made by precipitating nickel acetate solution with sodium carbonate. Contained 41,6% Ni.

Table 5. *Unmixed Catalysts in purified Resin Acid from Tall Oil. Heated in current of CO_2 for 3 periods of 30 min. successively.*

Resin acid (batch 6): M. P. 170—173°, acid No 186 mg KOH/g, iodine No 86 g J/100 g. Amount 1,511 g = 0.005 moles.

Exp. No	Catalyst: Kind	Catalyst: Concn. %	Catalyst: Concn. c:a	Temperature, °C	Time, min.	mg KOH/g: Acid No	mg KOH/g: Saponificat. No	Decrease in acid No by decarb.:n	Activity value of catalyst AV
63	—	—	—	283	30	171	186	15	—
64	—	—	—	283	60	168	179	18	—
65	—	—	—	283	90	161	172	25	—
66	$CaCl_2$	0,73	0,04	283	30	140	156	41	0,59
67	$CaCl_2$	0,73	0,04	283	60	135	149	46	0,33
68	$CaCl_2$	0,73	0,04	283	90	127	141	54	0,22
69	—	—	—	303	30	162	176	24	—
70	—	—	—	303	60	156	169	30	—
71	—	—	—	303	90	147	159	39	—
72a	ZrO_2	0,51	0,025	303	30	135	148	50	0,94
72b	ZrO_2	0,51	0,025	303	60	131	140	54	0,43
72	ZrO_2	0,51	0,025	303	90	129	133	57	0,22
73	UO_3	1,89	0,04	303	30	98	107	91	1,51
74	UO_3	1,89	0,04	303	60	91	103	98	0,77
75	UO_3	1,89	0,04	303	90	86	93	103	0,48
76	$MnCl_2 \cdot 4H_2O$	1,31	0,04	303	30	88	95	92	1,53
77	$MnCl_2 \cdot 4H_2O$	1,31	0,04	303	60	85	92	95	0,73
78	$MnCl_2 \cdot 4H_2O$	1,31	0,04	303	90	83	91	97	0,44
79	P-W-acid	0,20	0,0048	303	30	25	32	162	41,3
80	P-W-acid	0,20	0,0048	303	60	19	26	168	12,9
81	P-W-acid	0,20	0,0048	303	90	16	23	171	8,3
82	$HOSO_2Cl$	0,88	0,068	303	30	138	149	60	0,48
83	$HOSO_2Cl$	0,88	0,068	303	60	126	134	72	0,28
84	$HOSO_2Cl$	0,88	0,068	303	90	121	128	77	0,17

CeO_2 showed roughly the same effect as ZrO_2. $Co(NO_3)_2$ and Ni-formiate showed insignificant effects only. TiO_2, $Ti(SO_4)_2$, $SnCl_4$, $MnSO_4 . 4H_2O$, $CoCO_3$, Co-acetate, Ni-oxalate and $NiSO_4$ were without or almost without effect.

Table 6. *Some Iron Bearing Catalysts Used in Various Resin Acids, without CO_2.*

The resin acid batches 1 and 2 were the same as those used in the experiments of table 1.

Exp. No	Resin acid	Catalys: Kind	Concentration %	Concentration C:A	Temperature °C	Time, min.	mg KOH/g Acid No	mg KOH/g Saponificat. No	Decrease of acid No by decarb:n	Decrease of acid No by catalyst [12])
85	Batch 1	Fe	1,11	0,12	300	10	154	165	7	—
86	Batch 1	Fe	1,11	0,12	300	30	139	150	22	—7
87	Batch 2	Fe	0,062	0,0067	300	140	131	140	54	—20
88	Batch 2	Fe	0,093	0,010	300	140	118	127	66	—8
89	Batch 2	Fe	0,186	0,020	300	140	111	123	71	—3
90	Batch 2	Fe	1,11	0,12	300	140	78	84	83	+9
91	Batch 2	Fe	1,11	0,12	300	180	41	—	120	—
92	Remaining [1])	Fe	1,11	0,12	300	180	95	—[3])	31	—
93	Abietic	Fe	1,11	0,12	300	180	90	—[4])	55	—
94	Dehydroab.	Fe	1,11	0,12	300	180	94	—[5])	35	—
95	Batch 1	$FeCl_2$	1,67	0,080	280	30	135	135	40	—
96	Batch 1	$FeCl_2$	1,67	0,080	280	210	79	79	96	—
97	Batch 1	$FeCl_2$	0,84	0,041	300	30	143	155	38	+9
98	Batch 1	$FeCl_2$	1,67	0,080	300	30	110	125	65	+36
99	Batch 1	$FeCl_2$	1,67	0,080	300	140	61	65	114	+40
100	Remaining	$FeCl_2$	1,67	0,080	300	120	81	—[6])	55	—
101	Abietic	$FeCl_2$	1,67	0,080	300	120	62	—[7])	95	—
102	Dehydroab.	$FeCl_2$	1,67	0,080	300	120	65	—[8])	75	—
103	Batch 1	$FeCl_2$	1,67	0,080	300	280	13	13	162	—
104	Batch 1	$FeCl_2$	1,67	0,080	320	30	86	89	89	—
105	Batch 1	II Fe-resinate [2])	1,39	0,012	300	30	147	153	36	+7
106	Batch 1	II Fe-resinate	6,95	0,060	300	30	130	—	43	+14
107	Batch 1	II Fe-resinate	13,90	0,12	300	30	125	130	34	+5
108	Batch 1	II Fe-resinate	1,39	0,012	300	140	75	93	108	+34
109	Batch 1	II Fe-resinate	6,95	0,060	300	160	33	33	140	—
110	Batch 1	II Fe-resinate	13,90	0,12	300	160	60	61	99	—
111	Batch 1	II Fe-resinate	6,95	0,060	300	180	13	15	160	—
112	Batch 1	II Fe-resinate	13,90	0,12	300	180	50	57	109	—
113	Batch 1	II Fe-resinate	1,39	0,012	300	360	8	24	175	—
114	Batch 1	III Fe-resinate [9])	19,2	0,12	300	30	137	151	13	—16
115	Batch 1	III Fe-resinate	19,2	0,12	300	160	50	58	100	—
116	Batch 1	III Fe-resinate	19,2	0,12	300	180	44	52	106	—

[1]) Fraction of resin acids remaining free after heating 100 g of »pinabietic acid» for 190 min. at 300° C with 1,106 g Fe (p. 30). Acid No 145 mg KOH/g, iodine No 8,8 g J/100 g. — [2]) 8,06% Fe. — [3]) Iodine No 5 g J/100 g — [4]) 44 g J/100 g. — [5]) 2,3 g J/100. — [6]) 44 g J/100 g. — [7]) 39 g J/100 g. — [8]) 9 g J/100 g. — [9]) 5,78% Fe. — [10]) Value of d—b (p. 27).

Table 7. *Some Iron Bearing Catalysts in Purified Resin Acid from Tall Oil, in Current of CO_2.*

In the exp. 117—119 and 123—125 the resin acid was of the batch 6 (table 5) and in the exp. 120—122 of the batch 3 (table 1).

Exp. No	Catalyst Kind	Concentration %	Concentration C:a	Temperature, °C	Time, min.	mg KOH/g Acid No	mg KOH/g Saponificat. No	Decrease in acid No by decarb:n	Activity value of catalyst
117	$FeCl_2$	0,84	0,040	283	30	147	159	34	0,43[1])
118	$FeCl_2$	0,84	0,040	283	60	137	152	44	0,29[1])
119	$FeCl_2$	0,84	0,040	283	90	36	148	45	0,15[1])
120	Fe	0,093	0,010	300	140	126	129	58	0,0[2])
121	Fe	0,186	0,020	300	140	125	134	57	0,0[2])
122	Fe	1,11	0,12	300	140	83	84	78	0,03[2])
123	$Fe(NO_3)_3 \cdot 9H_2O$	1,78	0,040	303	30	80	85	97	1,64[3])
124	$Fe(NO_3)_3 \cdot 9H_2O$	1,78	0,040	303	60	73	88	104	0,83[3])
125	$Fe(NO_3)_3 \cdot 9H_2O$	1,78	0,040	303	90	65	76	101	0,47[3])

Fe (II)-resinate in concentrations of 1,4 to 10,4 % showed no or almost no calalytic effect at 300° C and this was the case also when using $FeSO_4 \cdot 7\ H_2O$ at 303° C in a concentration of 1,84 %.

[1]) Compared with the experiments 63—65, table 5.
[2]) » » » experiment 11, table 1.
[3]) » » » experiments 69—71, table 5.

Table 8. *Catalysts in Crude Tall Oil at 300° C, Without Current of CO_2.*

Tall oil sample 1: acid No 145, resin acid No [42]) 91 mg KOH/g, iodine No 185 g J/100 g, petroleum ether-insoluble matter 4,8%, unsaponifiable (petr. ether) 9,1%, petroleum-ether-soluble resin acids 50,0%, fatty acids 35,1%, acid No of resin acids 168, of fatty acids 175, volatile matter 0,6%, ash 0,04%, water soluble acids 0, viscosity Engler at 50° C 326, at 100° C 5,44. — Tall oil sample 2, from the same plant as sample 1: acid No 145, resin acid No 79 mg KOH/g.

Exp. No	Tall oil samole	Catalyst			Acid No, mg KOH/g, after heating, min.						Resin acid No after 360 min.	Iodine No after min.	
		Kind	Concentration		30	60	180	360	720	1080		360	1080
			%	C:A									
126	2	—	—	—	124	120	113	108	—	—	62	—	—
127	2	—	—	—	123	120	118	107	—	—	61	—	—
128	2	—	—	—	—	—	—	104	85	63	—	54	32
129	1	$CaCO_3$	1,0	0,077	114	108	101	90	—	—	54	—	—
130	1	$CaCO_3$	1,0	0,077	114	102	102	91	—	—	55	—	—
131	2	$CaCO_3$	1,0	0,077	—	—	—	78	50	21	—	57	36
132	2	H_2SO_4	1,0	0,079	—	107	102	84	—	—	—	—	—
133	2	H_3PO_4	1,0	0,118	—	68	60	45	30	19	—	57	38
134	1	Fe	1,5	0,208	106	92	68	34	—	—	23	—	—
135	1	Fe	1,5	0,208	104	87	67	36	—	—	30	—	—
136	1	Fe	1,5	0,208	—	—	—	33	24	11	—	49	28
137	1	$FeCl_2$	2,0	0,122	70	58	—	—	—	—	[1])	—	—
138	1	$FeCl_2$	2,0	0,122	66	56	—	—	—	—	[2])	—	—
139	2	$FeCl_3 . 6\ H_2O$	3,5	0,150	—	—	—	21	15	10	—	—	—
140	2	Ni-acetate	0,05	0,002	121	116	110	—	—	—	—	—	—
141	2	Ni-acetate	0,10	0,003	124	118	96	89	—	—	—	—	—
142	2	Ni-acetate	1,0	0,031	110	94	49	33	—	—	—	—	—
143	2	Ni-acetate	2,5	0,077	68	43	17	17	—	—	—	—	—
144	2	Ni-acetate	5,0	0,155	72	18	15	—	—	—	—	—	—
145	2	P-W-acid	0,2	0,006	104	92	67	41	22	—	—	—	—

The following materials were without or almost without effect even after 1080 min.: Na_2CO_3 (1.1%), K_2CO_3 (1,4%), CaO (0,6%), Ca $(OH)_2$ (0,7%) $MgCO_3$ (1,0%) showed roughly the same effect as $CaCO_3$.

[1]) After 60 min. 21. — [2]) After 60 min. 22.

Table 9. *Some Catalysts in Various Samples of Tall Oil, Without Current of CO_2.*

Crude Tall oil: sample 3, from the same plant as samples 1 and 2 (table 8). Acid No 149, resin acid No 67 mg KOH/g, unsaponifiable 8,2%. — Distilled tall oil: acid No 185, resin acid No 44.

Exp. No	Tall oil	Catalyst			Temperature, °C	Time, min.	mg KOH/g after exp.	
		Kind	Concentration				Acid No	Resin acid No
			%	C:A				
146	Crude	—	—	—	334	30	129	—
147	Crude	$ZnCl_2$	2,23	0,123	334	30	47	—
148	Crude	$NiCO_3$	2,27	0,144	334	30	67	—
149	Crude	$Ni(NO_3)_2 \cdot 6H_2O$	5,42	0,142	334	30	47	—
150	Crude	Ni-acetate	4,63	0,140	334	30	42	—
151	Crude	CaO	0,41	0,055	334	30	117	—
152	Crude	CaO + Ni-acetate	0,39 1,79	0,053 0,039	334	30	83	—
153	Crude	P-W-acid	2,46	0,074	334	30	35	—
154	Crude	P-W-acid	0,16	0,0048	300	60	134	66
155	Crude	P-W-acid	1,74	0,052	300	60	81	23
156	Distilled	Fe	1,80	0,196	333	60	115	42
175	Distilled	$FeCl_2$	3,45	0,165	333	60	109	9
158	Distilled	Ni-acetate	6,88	0,168	333	60	50	5
159	Distilled	P-W-acid	0,18	0,0044	333	60	96	5
160	Distilled	P-W-acid	0,17	0,0041	333	60	93	5

Table 10. *Catalysts and Other Admixed Substances in Pitch of Tall Oil, Without Current of CO_2.*

The pitch was heated before the experiments to 310° C in a fractionating vessel. Sample of pitch No 1: acid No 113 mg KOH/g, unsaponifiable 13,0%, resin acid 55,4%, fatty and other readily esterifiable acids 30,5%, acid No of »fatty acids» 135 mg KOH/g. — Acid No after heating to 310° C, but before decarb:n experiment 111 mg KOH/g, Time of heating 30 min.

Exp. No	Catalyst			Admixed subst.		Temperature, C	Acid No mg KOH/g	Decrease in acid No by decarb:n	Activity value of catalyst
	Kind	Concentration %	Concentration C:A	Kind	%				
161	$CaCl_2$	1,60	0,15	—	—	300	79	22	0,12
162	$ZnCl_2$	1,94	0,14	—	—	300	52	50	0,43
163	$FeCl_2.4\,H_2O$	2,81	0,14	—	—	300	63	37	0,29
164	$FeCl_2.4\,H_2O$	2,81	0,14	$Ca(OH)_2$	2,1	300	63[1])	3[2])	0
165	$FeCl_2.4\,H_2O$	2,81	0,14	$CaCO_3$	1,4	300	69[3])	14[4])	0,04
166	$FeCl_2.4\,H_2O$	2,81	0,14	Na_2CO_3	1,5	300	90	—8	0
167	$FeCl_2.4\,H_2O$	2,81	0,14	—	—	320	45	55	0,48
168	$FeCl_2$	1,80	0,14	—	—	300	66[5])	35	0,27
169	$FeCl_2$	1,80	0,14	CH_3CO_2Na	2,0	300	87[6])	12	0,02
170	$FeCl_2$	1,80	0,14	—	—	310	36	65	0,59
171	$FeCl_2$	1,80	0,14	NH_3 [7])	0,25	310	55	37	0,29
172	$FeCl_2$	1,80	0,14	$(NH_4)_2CO_3$[8])	0,20	310	60[11])	38	0,30
173	$FeCl_2$	1,80	0,14	$(NH_4)_2CO_3$[9])	0,50	310	66[12])	29	0,20
174	$FeCl_2$	1,80	0,14	$(NH_4)_2CO_3$[10])	0,80	310	60[13])	31	0,22
175	$FeCl_3$	2,30	0,21	—	—	300	73	20	0,07
176	P-W-acid	0,50	0,02	—	—	300	88	20	0,75

The following substances showed no or almost no catalytic effect at 310° C: ferrous oxalate, $AlPO_4$, CaO, HCl. Experiments with $FeCl_2$ (1,8%) with admixtures of Zn-dust (2,0 %) respectively ZnO (1,2 %) showed no increase of the effect of the iron chloride.

[1]) At first the pitch was heated with the $Ca(OH)_2$ to 300° C. The acid No was then 95. Thereafter the $FeCl_2 \cdot 4\,H_2O$ was added. — [2]) The heating was continued further 30 min. The acid No was thereafter 51. — [3]) The pitch was at first heated with the $CaCO_3$ to 300° C. The acid No was then 95. — [4]) The heating was continued further 30 min. The acid No was thereafter 53. — [5]) The heating was continued further 30 min. The acid No was thereafter 48. — [6]) Acid No before heating 112. — [7]) As concentrated water solution. — [8]) The distillate was titrated (methyl orange). Content of acid, calculated as HCl, 0.06% of the pitch. — [9]) The distillate contained acid, as HCl, 0,03 % of the pitch. — [10]) The distillate was free from HCl. — [11]) The heating was continued further 30 min. The acid No was thereafter 47. — [12]) The heating was continued further 30 min., the acid No being thereafter 57. — [13]) Further heating 30 min. : acid No 51.

Table 11. *Catalysts and Other Admixed Substances in Pitch of Tall Oil, in Current of CO_2.*

Experiments of type 2 (page 25). Sample of pitch No 1 (table 10). Amount of pitch 0,500 g. The pitch in some cases was heated before the experiment to 310° C. *Additions, sec p. 35.*

Exp. No	Pitch original (0) or heated (H)	Catalyst			Admixed subst.		Temperature °C	Time min.	Acid No, mg in KOH/g	Gas, insoluble in KOH	Decrease in acid No by decarb:n
		Kind	Concentration %	Concentration C:A	Kind	%					
177	O	—	—	—	—	—	300	30	103	1,2	10
178	O	$Ni(NO_3)_2 \cdot 6\,H_2O$	1,00	0,034	—	—	300	30	89	6,9	21
179	H	$Ni(NO_3)_2$	0,31	0,017	—	—	300	30	101	1,7	9
180	H	$Ni(NO_3)_2$[1])	0,63	0,035	—	—	300	30	—	6,4	—
181	H	$Ni(NO_3)_2$[2])	0,63	0,035	—	—	300	60	—	10,8	—
182	H	$Ni(NO_3)_2$[3])	0,63	0,035	—	—	300	90	54	14,6	54
183	H	$Ni(NO_3)_2$	0,63	0,035	H_2 [4]	—	302	30	78	6,7	30
184	H	$Ni(NO_3)_2$	0,63	0,035	Fe-dust	1,00	301	30	78	6,4	9
185	H	$Ni(NO_3)/_2$	0,63	0,035	Cu-dust	0,15	299	30	87	7,4	18
186	H	$Ni(NO_3)_2$	0,63	0,035	Na_2CO_3	0,31	300	30	89	2,6	15
187	H	$Ni(NO_3)_2$	0,63	0,035	Na_2S	0,50	300	30	98	1,6	2
188	H	—	—	—	$CuCO_3$	0,30	300	30	99	1,0	9
189	H	$Ni(NO_3)_2$	0,63	0,035	$CuCO_3$	0,30	300	30	69	7,6	36
190	H	$NiCO_3$	0,40	0,034	—	—	300	30	100	3,8	7
191	H	$NiCO_3$	0,40	0,034	$CuCO_3$	0,30	300	30	90	5,3	14
192	H	—	—	—	$Cu(NO_3)_2$	0,64	300	30	99	1,0	9
193	H	—	—	—	$Cu(NO_3)_2$	3,00	300	30	101	1,8	—2
194	H	$Ni(NO_3)_2$	0,63	0,035	$Cu(NO_3)_2$	0,46	300	30	83	7,4	23
195	H	$Ni(NO_3)_2$	0,63	0,035	$Cu(NO_3)_2$	0,16	300	30	96	6,5	11
196	O	Ni-acetate	0,42	0,017	—	—	300	30	94	1,7	18
197	H	Ni-acetate	0,42	0,017	—	—	300	30	99	2,9	11
198	H	Ni-acetate	0,85	0,035	—	—	300	30	88	7,2	21
199	H	Ni-acetate	0,85	0,035	—	—	300	30	86	7,1	23
200	H	$ZnCl_2$	3,00	0,22	—	—	300	30	46	8,7	50
201	H	$FeCl_2 \cdot 4\,H_2O$	3,00	0,15	—	—	301	30	70	4,2	29
202	H	$FeCl_3$	3,60	0,34	—	—	302	30	54	5,8	29
203	H	$FeCl_3 \cdot 6\,H_2O$	3,00	0,17	—	—	302	30	85	3,0	10
204	H	$Fe(NO_3)_3 \cdot 9\,H_2O$	3,00	0,11	—	—	303	30	89	2,9	11

[1]) Compare exp. No 180 b (p. 35). — [2]) This experiment is a continuation of exp. 180. — [3]) Continuation of No 181. — [4]) A current of H_2 was passed through the reaction mixture for 5 min. at 301° C.

Table 12. *Sulfonic Acids as Catalysts in Purified Resin Acid from Tall Oil, in Current of CO_2.*

Substrate: purified resin acid from tall oil, batch 6 (table 5), 0,005 moles. Temperature 303° C.

Exp. No	Catalyst: Kind	Catalyst: Concentration %	Catalyst: Concentration C:A	Time, min.	mg KOH/g: Acid No	mg KOH/g: Saponific. No	Decrease in acid No by decarb.:n	Activity value of catalyst
205	methanilic acid	1,14	0,020	30	54	60	130	4,77
206	» »	1,14	0,020	60	30	37	154	2,79
207	» »	1,14	0,020	90	18	23	166	1,90
208	p-toluene sulfonic acid	0,88	0,016	30	41	48	146	6,86
209	» »	0,88	0,016	60	29	33	158	3,60
210	» »	0.88	0,016	90	22	28	165	2,36
211	p-toluene sulfochloride	1,26	0,020	30	82	88	105	3,65
212	» »	1,26	0,020	60	73	78	114	1,89
213	» »	1,26	0,020	90	71	75	116	1,15
214	Cymene sulfonic acid	1,16	0,016	30	99	107	88	3,60
215	» » »	1,16	0,016	60	83	88	104	2,08
216	» » »	1,16	0,016	90	74	79	113	1,39
217	Naphtol yellow S (acid)	2,08	0,022	30	65	69	117	3,80
218	» »	2,08	0,022	60	53	58	129	2,02
219	» »	2,08	0,022	90	45	51	137	1,34
220	Camphor sulfonic acid	1,44	0,019	30	110	119	77	2,51
221	» » »	1,44	0,019	60	106	115	81	1,21
222	» » »	1,44	0,019	90	101	108	86	0,74
223	Dehydroabietic acid sulfonate	2,64	0,021	30	125	132	66	1,80
224	» » »	2,64	0,021	60	123	131	68	0,81
225	» » »	2,64	0,021	90	119	127	72	0,47

The following materials were inactive or almost inactive: the o- and p-anilinsulfonic acids (orthanilic and sulfanilic acid), sulfanilamide, amidophenol-4-sulfonic acid, pyrogallol-4-sulfonic acid, the l-naphtol-4 and -5 sulfonic acids, 2-naphtol-6-sulfonic acid, the l-naphtol-4-8- and -3-8-disulfonic acids.

Table 13. *Decarboxylations of Resin Acids. Complete Experiments.*

Experim. of type 3 (p. 5). Amount of resin acid 15,112 g = 0,050 moles, except at exp. 236, where 15,206 g of »oxy acids» from pine tar were used. Notes to table 13, see p. 56.

Experiment No	226	227	228	229	230	231	232	233	234	235	236	237	238	239	240
Resin acids, batch	7[1])	7[1])	7[1])	7[1])	3[2])	1[2])	8[3])	1[2])	9[3])	9[3])	Oxy-acids[4])	8[5])	5[6])	7[1])	8[5])
Catalyst:					II										
Kind	—	—	Fe	Fe	Fe-resinate	$FeCl_2$	$FeCl_2$	$FeCl_2$	$FeCl_3$ $6\,H_2O$	$FeCl_2$ $6\,H_2O$ pretreat[17])	$FeCl_3$ $6\,H_2O$	Ni-acet.[27])	Ni-acet.	Ni-acet.	P-W-acid
Concentration, %	—	—	1,11	1,11	10,3	1,68	1,68	1,68	3,59	3,59	2,36	0,72	0,72	0,72	0,02
» ,C:A	—	—	0,12	0,12	0,094	0,080	0,080	0 080	0,12	0,12	0,095	0,017	0,017	0,017	0,0048
Temperature, ° C	352	(About 380[8])	306	304	300	280	300	300	296	300	300	302	306	350	302
Time of heating min.	129	12	192	158	140	210	140	280	120	65	60	508	60	49	120
Decrease in weight, g	1,962	1,854	0,977	1,468	—	—	1,773	—	2,58	—	1,657	2,083[9])	0,888	2,498	1,888
Developed gas ml:												[14])			
in first 30 min.	420	—	175	350	228	460	630	606	700	685	395	280	326	970	680
in 60 »	660	—	390[10])	480	310	580	770	834	810	790	465	530	512	—	900
in 120 »	880	—	530	610	413	680	860	1 098	945	—	—	660	—	—	1 000
in 180 »	—	—	630	—	—	703	—	1 310[11])	—	—	—	680	—	—	—
total (760 mm, 20°C)	900	850	645	680	445	750	883	1 416	945	800	465	1068	512	1200	1000
% of air-free gas:		[12])	[13])									[15])			
CO_2	24,7	13,3	9,5	69,6	63,6	46,8	47,6	36,4	42,8	41,3	56,6	15,6	13,6	20,3	29,4
CO	58,0	75,8	78,5	16,0	14,0	44,9	47,7	56,5	51,0	49,0	24,6	69,5	65,2	65,1	67,1
H_2	5,7	2,8	4,3	9,2	7,5	3,3	2,4	2,6	2,3	4,1	1,3	11,4	12,5	7,9	0,3
$C_n\,H_{2n}$	3,3	2,1	1,5	2,0	—	—	0,8	1,2	1,0	1,1	6,4	1,3	8,7	2,7	1,7
CH_4	8,3	6,0	6,2	3,2	12,7[16])	4,3[17])	1,5	3,3	2,9	3,7	6,3[18])	2,2	9,0	4,0	1,5
Acid No of residue	59	97	79	—	118	80	72	13	59	68	81	75	124	28[19])	60
Saponific No of »	—	—	21	—	118	80	75	13	69	69	—	79	126	—	64
Acid No of residue															
calc: d from gas anal.	81	—	89	—	127	77	48	—	—	53	—	52	129	30	—
Analysis of residue:															
unsaponifiable, %	44,3	42,9	29,9	—	—	—	55,1	—	—	61,2	24,8	55,8	28,4	—	64,7
» iodine No	59	70	59	—	—	—	90	—	—	52	38	53	—	—	84
acids (saponifiab.)%	50,4	52,9	65,4	—	—	—	41,4	—	—	—	68,2[26])	40,6	72,3	—	31,0
» ,acid No	146	165	159	—	—	—	185[20])	—	—	—	122[21])	180[22])	171	—	181[22])
» , iodine No	12	24	11	—	—	—	6[23])	—	—	9	20	19[24])	—	—	12[25])
» , $[\alpha]_D^{18}$	+52,9	+ 47,1	41,3	—	—	—	+49,1	—	—	—	—	+ 48,3	—	—	+55,7

Notes to table 13, see p. 52.

[1]) M. P. 168—172°. — [2]) Table 1. — [3]) M. P. 165—172°, iodine No 94 g J/100 g. [4]) »Oxy acids» from pine tar, acid No 158 mg KOH/g, p. 28. — [5]) M. P. 165—172,5°, acid No 187, saponificat. No also 187 mg KOH/g $[\alpha]_D$ + 0,8°, iodine No 95 g J/100 g — [6]) Table 3. — [7]) The ferric chloride was heated before the experiment with its own weight of neutral lubricating oil from pine tar for one hour at 170° C. After this pretreatment 68 % of the chlorine of the iron chloride remained in the catalyst, whereas 26 % was found in the evolved vapors, which were passed through water (titration with 0,5 n KOH using methylorange as indicator). The rest (5,6%) of the chlorine apparently remained as drops of hydrochloric acid in the upper part of the reaction vessel. — [8]) »Pinabietic acid» was boiled in a fractionating vessel at atmospheric pressure. The temperature in the distilling vapour rose to 364° at the end of the boiling process. The temperature in the boiling fluid was not measured, but it must have been about 380° C. — [9]) After 208 min. 1 407 g. — [10]) The Fe dissolved after 45 min. — [11]) In 240 min. 1 400 ml. — [12]) Analysis of the gas collected until the temperature of the vapour had risen to 350° C. — [13]) Gas collected duri ng rise of temperature in vapour from 350° to 364° C. — [14]) Analysis of gas evolved during the first 208 min. — [15]) Gas evolved during the last 300 min. — [16]) Further 2,2% of homologies of methane, calculated as propane. — [17]) Further 0,7 % of homologies of methane calculated as propane. — [18]) Further 4,7 % of homologies of methane calculated as propane. — [19]) Iodine No 28 g J/100 g. — [20]) Saponification No 188 mg KOH/g. — [21]) Saponification No 193 mg KOH/g. — [22]) Saponification No 184 mg KOH/g. — [23]) Diene No (8 h. 160°) 22 g J/100 g. — [24]) Diene No 32 g J/100 g. — [25]) Diene No 20 g J/100 g. — [26]) Further 5,3 % of dark, solid matter, insoluble in ether. — [27]) The reaction mixture was dissolved in 100 ml of benzene-alcohol 1 : 1. A grey precipitate was filtered in an atmosphere of carbon dioxide and dried in vacuo at room temperature. Its weight was 87,2 % of the amount of metallic nickel theoretically obtainable from the used amount of nickel acetate. A sample of the precipitate ignited in a crucible was found to show an increase in weight of 21,3 %.

Table 14. *Distillation of the Unsaponifiable Matter of the Residue from Some Decarboxylation Experiments.*

Exp. No. (table 13)	Catalyst	Boiling point		$d\frac{18}{4}$	%	% C	% H
		mm Hg	° C				
232	$FeCl_2$	0,16	129—140	0,964	11,6	—	—
»	»	0,16	140—144	0,968	60,8	88,55	11,13
»	»	0,16	144—163	0,983	8,3	88,56	10,89
»	»	Residue and loss		—	19,3	88	—
237	Ni-acetate	0,18	139—147	0,983	28,5	—	—
»	»	0,18	147—149	0,983	40,7	89,05	10,99
»	»	0,20	150—180	1,010	7,2	—	—
»	»	Residue and loss		—	23,6	—	—
240	P-W-acid	0,18	85—105	0,972	17,3	—	—
»	»	0,34	133—143	0,973	30,0	88,65	11,26
»	»	0,36	145—153	0,974	15,7	—	—
»	»	0,35	156—170	0,988	18,4	—	—
		Residue and loss		—	18,6	—	—
Abietene $C_{19}H_{30}$		0,1	143—145	0,967	—	88,29	11,71
Abietine $C_{19}H_{28}$		10	191—193	0,974	—	88,99	11,01
Retene $C_{18}H_{18}$		11	216	—	—	92,25	7,75
Octohydroretene		10	163—165	0,958	—	89,18	10,82
Hexahydroretene		10	175—177	0,980	—	89,91	10,09

Table 15. *Zinc Chloride at Varying Temperatures and in Varying Concentrations in Purified Resin Acid from Tall Oil.*

Current of CO_2. Resin acid of batch 6 (table 5), amount 1,511 g.

Exp. No	Concentration of $ZnCl_2$		Temperature, C	Time, min.	mg KOH/g		Decrease in acid No by decarb:n
	%	C:A			Acid No	Saponificat. No	
241	4,50	0,20	151	30	178	189	—19
242	4,50	0,20	151	60	174	187	—15
243	4,50	0,20	151	90	171	176	—12
244	4,50	0,20	171	30	150	165	9
245	4,50	0,20	171	60	129	141	30
246	4,50	0,20	171	90	124	138	35
247	0,90	0,04	201	30	145	158	36
248	0,90	0,04	201	60	141	147	40
249	0,90	0,04	201	90	139	146	42
250	4,50	0,20	201	30	100	111	59
251	4,50	0,20	201	60	98	104	61
252	4,50	0,20	201	90	95	98	58
253	0,22	0,01	262	30	176	184	9
254	0,22	0,01	262	60	164	172	21
255	0,22	0,01	262	90	162	168	23
256	0,45	0,02	262	30	159	170	24
257	0,45	0,02	262	60	148	164	35
258	0,45	0,02	262	90	142	152	41
259	0,90	0,04	262	30	92	107	89
260	0,90	0,04	262	60	84	90	97
261	0,90	0,04	262	90	76	88	105
262	1,80	0,08	262	30	75	89	100
263	1,80	0,08	262	60	62	66	113
264	1,80	0,08	262	90	54	65	121
265	0,90	0,04	283	30	72	94	109[1])
266	0,90	0,04	283	60	63	78	118[2])
267	0,90	0,04	283	90	41	50	140[3])

[1]) Activity value of catalyst 2,11
[2]) » » » » 1,12
[3]) » » » » 0,86

Table 16. *Zinc Chloride at Varying Temperatures and in Varying Concentrations in Crude Tall Oil.*

Current of CO_2. Tall oil: sample 4, from the same plant as the samples 1—3 (tables 8 and 9). Acid No 152 mg KOH/g.

Exp. No	Concentration of $ZnCl_2$		Temperature, °C	Time, min.	mg KOH/g			Decrease in acid No by de-carb:n
	%	C:A			Acid No	Saponific No	Resin acid No	
268	0,75	0,04	206	30	146	—	—	2
269	0,75	0,04	206	60	143	—	—	5
270	0,75	0,04	206	90	142	—	—	6
271	0,75	0,04	266	30	109	—	—	39
272	0,75	0,04	266	60	103	—	—	45
273	0,75	0,04	266	90	99	—	—	49
274	0,75	0,04	277	30	101	—	—	47
275	0,75	0,04	277	60	86	—	—	62
276	0,75	0,04	277	90	80	—	—	68
277	0,38	0,02	287	30	121	141	69	29
278	0,38	0,02	287	180	83	96	29	67
279	0,75	0,04	287	30	94	101	35	54
280	0,75	0,04	287	60	78	91	29	70
281	0,75	0,04	287	90	75	87	27	73
282	1,50	0,08	287	30	69	83	32	75
283	1,50	0,08	287	90	59	70	25	85
284	2,27	0,12	287	30	56	—	—	84
285	2,27	0,12	287	60	49	—	—	91
286	2,27	0,12	287	90	44	—	—	96
287	0,75	0,04	300	30	82	87	—	66
288	0,75	0,04	300	60	69	75	—	79
289	0,75	0,04	300	90	59	68	—	89

Table 17. *Influence of the Presence of Calcium Hydroxide on the Effect of Some Catalysts in Resin Acid from Tall Oil.*

Without current of CO_2. Time of heating 60 min. Temperature 300° C. In the cases where Ca $(OH)_2$ was used, the resin acid was heated with the lime alone 5 min. at 300° C before the experiment.

Exp. No	Resin acid	Catalyst			$Ca(OH)_2$ %	Decrease in weight, % of resin acid	Acid No	Decrease in acid No by decarb:n	Activity value of catalyst
		Kind	Concentration						
			%	C:A					
290	Crude[1])	—	—	—	1,40	1,76	154	8	—
291	»	$FeCl_3 . 6 H_2O$	2,00	0,067	—	9,22	92	82	0,50
292	»	$FeCl_3 . 6 H_2O$	2,00	0,067	1,40	11,64	73	77	0,46
293	»	$FeCl_3 . H_2O$	1,33	0,067	—	9,72	86	89	0,54
294	»	$FeCl_3 . H_2O$	1,33	0,067	1,40	10,14	79	72	0,43
295	»	$FeCl_3 . H_2O$ +resin acid [2])	1,3 1,3	0,067	—	7,30	110	63	0,37
296	»	$FeCl_3 . H_2O$+ lubricat. oil[3])	1,3 1,3	0,067	—	8,78	85	88	0,54
297	M.P.160-163°	Fe	1,11	0,12	—	10,48	118	43	0,13
298	»	Fe	1,11	0,12	1,40	11,38	109	28	0,08
299	»	Ni-acetate	0,25	0,006	—	15,29	95	90	6,15
300	»	Ni-acetate	0,25	0,006	1,40	12,30	91	70	4,65
301	»	P-W-acid	0,06	0,0014	—	7,47	115	71	20,2
302	»	P-W-acid	0,06	0,0014	1,40	9,71	92	70	19,9
303	From pine tar	—	—	—	—	4,4	165	14	—
304	» » »	$FeCl_3 . 6 H_2O$	2,20	0,076	—	12,5	123	43	0,18
305	» » »	$FeCl_3 . 6 H_2O$	2,36	0,082	1,40	14,7	117	24	0 04
306	» » »	$FeCl_3 . 6 H_2O$ + resin acid[4])	2,47 2,48	0,086	—	13,2	135	30	0,09
307	» » »	$FeCl_3 . 6 H_2O$ + resin acid	2,41 2,37	0,084	1,37	11,0	104	37	0,13
308	» » »	$FeCl_3 . 6 H_2O$ + lubricat oil	2,28 2,43	0,079	—	11,3	135	26	0,07
309	» » »	$FeCl_3 . H_2O$ + lubricat. oil	2,44 2,38	0,085	1,48	12,5	120	15	0,01
310	Oxy acids from pine tar[5])	—	—	—	—	7,14	99	59	—
311	» » »	$FeCl_3 . 6 HO$	2,12	0,071	—	9 57	60	87	0,21
312	» » »	$FeCl_3 . 6 H_2O$	2,35	0,079	1,37	12,3	53	67	0,05

[1]) Crystallized, commercial resin acid from tall oil from the plant of Enso-Gutzeit-Kotka. — [2]) $FeCl_3 . H_2O$ was heated before the experiment with its own weight of resin acid to about 170°. — [3]) The $FeCl_3 . H_2O$ was heated before the experiment with its own weight of lye-washed lubricating oil from pine tar to about 170°. — [4]) The chloride ion content of the reaction mixture was determined after the experiment by heating with lime. The mixture contained 41,5 % of the original amount of Cl in the added iron chloride. — [5]) Acid No 158 mg KOH/g, p. 28.

Table 18. *Catalysts and Other Admixed Substances in Purified Resin Acid from Tall Oil, in Current of CO_2.*

The exp. 313—319 are made with the same resin acid and even in other respects in the same way as the experiments reported in the table 4. The exp. 320—326 were correspondingly made as the experiments reported in table 5. — The values of mg KOH/g of the exp. 320—326 are means of two pairs of values obtained on the one side in experiments without mixing, on the other in experiments by mixing with a glass rod. The differences of the values were mostly only 0—4, in one case (exp. No 323) 8 mg KOH/g.

Further experiments showed that an admixture of 0,24 % nickel acetate or 0.14 % of pyrocatechine did not have any effect worth mentioning in decarboxylation of resin acid with tungstic acid.

Exp. No	Catalyst			Admixed subst.		Temperature °C	Time min.	mg KOH/g		Gas, insoluble in KOH, ml	Decrease in acid No by decarb.n
	Kind	Concentration		Kind	%			Acid No	Saponific No		
		%	C:A								
56	$WO_3 . H_2O$	0,17	0,004	—	—	308	30	118	127	33,0	67
313	$WO_3 . H_2O$	0,17	0,004	Salicyl.acid	0,36	311	30	134	142	24,6	52
314	$WO_3 . H_2O$	0,17	0,004	dl-alanine	0,24	312	30	154	165	12,9	31
52	Ni-acetate	1,65	0,04	—	—	310	30	149	156	28,0	29
315	Ni-acetate	1,65	0,04	Sorbite	1,61	310	30	132	143	31,0	43
316	Ni-acetate	1,65	0,04	Betaine	3,10	311	30	96	103	62,8	76
317	Ni-acetate	1,65	0,04	dl-alanine	2,36	310	30	110	115	50,9	63
318	Ni-acetate	1,65	0,04	dl-alanine	0,59	311	30	113	120	55,1	64
37	Ni-acetate	8,21	0,20	—	—	306,5	30	90	98	—	61
319	Ni-acetate	8,21	0,20	dl-alanine	11,8	307	30	44	59	—	86
320	Ni-acetate	1,65	0,04	—	—	303	30	75	78	—	104
321	Ni-acetate	1,65	0,04	—	—	303	60	64	71	—	115
322	Ni-acetate	1,65	0,04	—	—	303	90	60	69	—	119
323	Ni-acetate	1,65	0,04	dl-alanine	1,99	303	30	75	82	—	100
324	Ni-acetate	1,65	0,04	dl-alanine	1,99	303	60	42	53	—	133
325	Ni-acetate	1,65	0,04	dl-alanine	1,99	303	90	37	42	—	138
326	—	—	—	dl-alanine	0,50	303	30	166	—	—	19

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Litteratur.

Fysikalisk-kemiska räkneuppgifter av Lars Gunnar Sillén, Paul W. Lange och C. Olof Gabrielson. Almqvist och Wiksells Akademiska handböcker, Hugo Geber, 1948.

Med denna bok fylles ett stort aktualitetsbehov på ett synnerligen tillfredsställande sätt. Aktualitetsbehovet tillgodoses såväl med uppgifter från fysikaliska kemiens nyaste betydelsefulla terrängvinningar som även med de nya aspekter varunder de gamla klassiska problemen alltsedan *Arrhenius'* dagar behandlas. Ett slående intryck av denna forskningsgrens utveckling fick anmälaren vid jämförelse av problemen i denna bok med de uppgifter han i tiden själv fick brottas med under den kanske allra första kursen i fysikaliskt-kemiskt räknande som hållits, anordnad 1908 av *Abegg* och *Sackur*, uppgifterna sedermera i tryck utgivna i Sammlung Göschen. Även denna samling var en gång aktuell och fyllde väl den tidens krav, men vilken skillnad mellan då och nu både betr. stoffets omfång och dess behandling. Ja den fysikaliska kemien har nog sedan dess blivit betydligt »svårare» och de nu framlagda uppgifterna fordrar otvivelaktigt, såsom författarena uttrycka sig, en del tankemöda.

Men mödan får sin belöning. Det finnes intet bättre sätt att inträngа i den fysikaliskt kemiska begreppsvärlden än att lösa räkneuppgifter. En viktig förutsättning härför är att uppgifterna nära ansluta sig till verkliga forskningsproblem och därur framgångna experimentella mätningar, varom författarena även varit särskilt angelägna. Detta är en av bokens främsta förtjänster. De flesta uppgifterna äro försedda med hänvisningar till de tidskriftsuppsatser, varifrån de tagits och förf. uttalar det allvarliga hoppet att läsaren själv skall uppsöka källskrifterna. »I allmänhet skall han därvid finna ej blott det rätta svaret och huru man räknar sig fram till det utan även huru mätningarna gingo till och varför man valt just det arbetssättet.»

De förkunskaper, som erfordras äro i fysik ungefär vår approbaturskurs och i matematik i huvudsak kännedom om differential- och integralräkningens grunder och så givetvis kännedom av stoffet ifrån motsvarande ställen i läroboksliteraturen. För att för läsaren underlätta inhämtandet av detta, alltså påvisa vad han bör lära sig behärska, har till ledning i början av varje kapitel sammanställts de nödvändiga definitionerna och formlerna samt materialet i övrigt ordnats så, att intet tal fordrar kunskaper, som ges i ett senare kapitel. De mera omfattande uppgifterna utgöra i själva verket envar en mindre självständig forskningsuppgift för sig.

Räknandet av dessa tal är sålunda på ett förträffligt sätt egnat ej blott till inhämtande av levande kunskap utan framför allt till att underlätta den mödosamma uppskolningen till behandling av egna forskningsproblem. Boken kan på det allra bästa rekommenderas för det högre och högsta undervisningsstadiet.

Kurt Buch.

Förening bildad på livsmedelsforskningens och livsmedelskontrollens område.

År 1947 grundades i Helsingfors en förening, som antog namnet *»Elintarviketutkijain Seura»*. Föreningens ändamål är att vara ett samlande organ för kemister, läkare och veterinärer, vilka äro sysselsatta på gebitet för livsmedelsforskning och -kontroll. Föreningen hade sitt första årsmöte den 18 mars 1948 i Statens tekniska forskningsinstituts föreläsningssal. Förhandlingarna leddes av föreningens ordförande prof. J. Tikka. Efter det mötet behandlat föreningens inre angelägenheter höll mag. T. Weijola ett föredrag benämnt »Hektolitervikten som grund för prissättningen av spannmål». Därpå följde ett diskussionsunderlag om dricksvattenfrågan i vårt land, framfört av mag. V. I. Salminen. Föredragaren betonade, att dricksvattnet i vårt land tages ofta från ur hygienisk synpunkt förkastliga brunnar och vattentäkter. På grund av anförandet beslöt mötet på förslag av medicinalrådet H. Sarkko att vända sig med en skrivelse till Statsrådet, vari skulle föreslås tillsättandet av en kommitté för utredandet av vattenfrågan i vårt land i hela dess vidd.

Kemikalier
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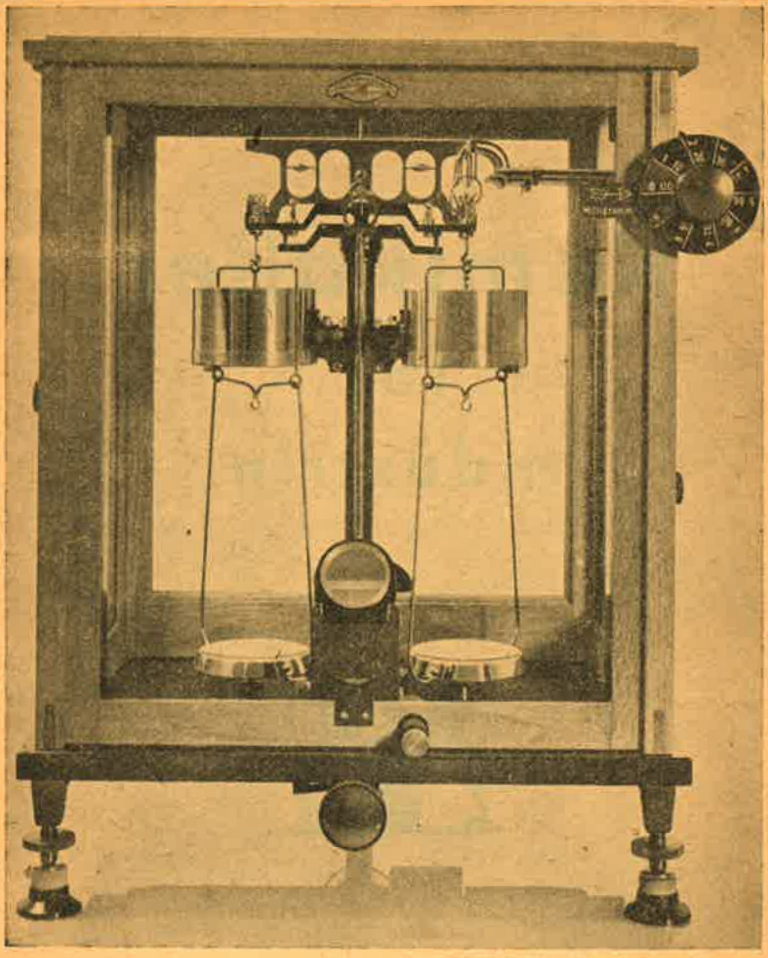

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