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9. Other Synthetic Lubricating Oils, (Cont'd.)

the triethanol amine salts can be varied widely by the use of fatty acids of varying molecular weight. A sample of this water-soluble oil was obtained and forwarded to the Naval Research Laboratory.

10. Additives to Lubricating Oils:

With the necessity of supplying lubricants to new and exacting uses, and with the ever present urge to upgrade low quality materials to increase the volume of lubricants, it was expected that Germany had given attention to the development of additives. It was found that many companies had been studying additives and that, parallel to the situation in America, hundreds of compounds had been synthesized and tested. From this mass of research there were developed some new compounds that were being used commercially and which perhaps could be useful to America,

The use of inhibitors and additives in lubricating oils was less extensive in Germany than it is today in America. Mineral oils were used uninhibited, and no inhibitors or additives were used in the synthetic lubricating oils or in the aircraft oils containing esters. As stated before, no special attention was given to diesel oils, and again no inhibitors or additives were used in them.

The use of additives was limited therefore to special oils but since it was the practice to specify special oils for a great many needs, there were large numbers of special compounded oils marketed. Natural fats and oils were used, but their shortage encouraged the development of substitutes. The shortage of natural esters, for example, was one of the reasons for the study of synthetic esters which lead to the extensive development previously described.

Some outstanding new additives are described briefly below, classed according to their effect on lubricating oil properties.

(a) Oxidation Inhibitors:

An oxidation inhibitor developed by I. G. - Leuna was claimed to be the most effective one that had been tested for improving

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10. Additives to Lubricating Oils, (a) (Cont'd.)

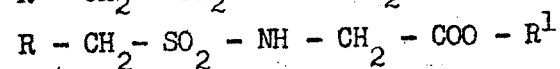
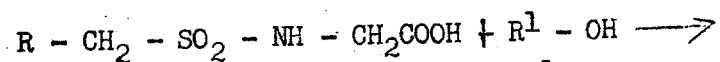
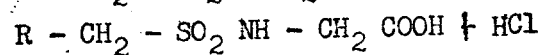
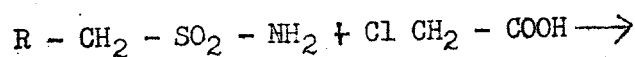
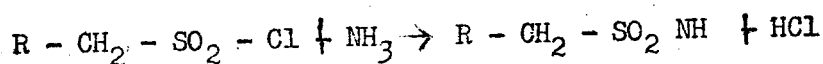
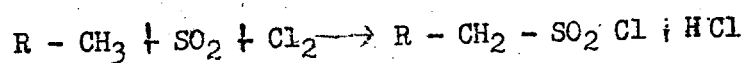
the stability of polyethylene-mineral oil mixtures. No test data were found, but this compound was the subject of patent applications, and was repeatedly discussed in interviews. It was not used in commercial practice. The material is a tin compound, made by the following synthesis:

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10. Additives to Lubricating Oils, (Cont'd.)

(b) Corrosion Inhibitors:

A compound developed by I. G. - Leuna, known as KSE (Korrosionsschutzester), shows very good corrosion resisting properties. In a cutting oil study a soap that was being tested was observed to protect iron surfaces against rusting. An ester of the acid was then prepared and studied as a lubricating oil ingredient. Extensive test data and field experience were accumulated, and this compound was being manufactured and included in several special machine oils, torpedo oils, and weapon oils. The compound is prepared from a normal C_{12} to C_{18} paraffin, obtained in Germany by selecting a fraction of Fischer-Tropsch liquid. The synthesis was then carried out in the following steps:

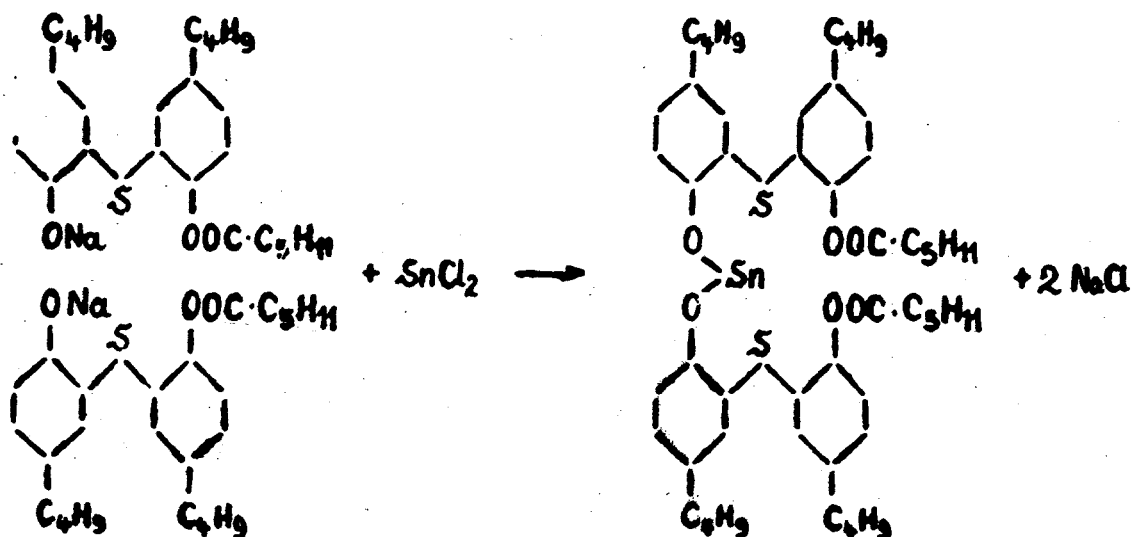
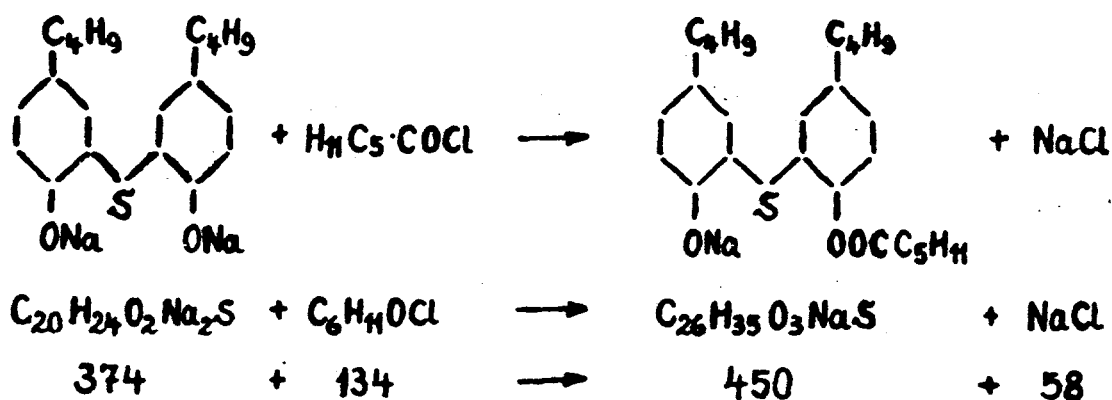
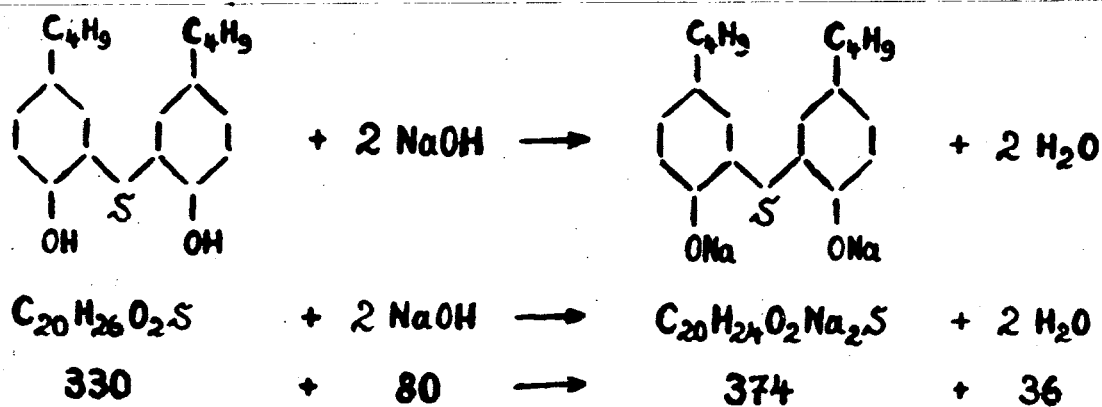


(R is C_{12} to C_{18} and R^1 is from C_4 to C_{16})

The reaction of the paraffin with SO_2 and Cl_2 is catalyzed with ultraviolet light. The NH_3 and the chloroacetic acid reactions proceed without catalysts.

As an emulsifying soap in cutting oils, the soap usage is 4 to 6 percent weight. For the other applications, the ester is used in concentrations of about 3 percent weight.

Reaktionsschema für Inhibitor (continued)



10. Additives to Lubricating Oils, (b) (Cont'd.)

Test data have shown that 3 percent of the ester in a lubricating oil will reduce iron corrosion rate to 2 percent of that observed with uninhibited oil. Although particularly effective for iron protection, zinc, aluminum, and lead also show greatly decreased corrosion rates from the use of this material.

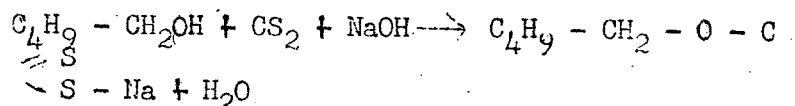
A sample of several gallons of KSE was obtained and forwarded to the Naval Research Laboratory in Anacostia, D. C.

(c) Extreme Pressure Additives:

An extreme pressure agent allows movement of one metal surface over another under extreme load conditions without seizure of the metals occurring. To act in such a capacity, an agent must effect a reduction in friction by providing some moving layer between the two (2) surfaces. Most extreme pressure additives accomplish this effect by reacting irreversibly with the surfaces, forming a metal compound which rubs off the metal and provides a moving layer which departs from the surfaces with less friction than that accompanying the motion of one pure metal surface over the other.

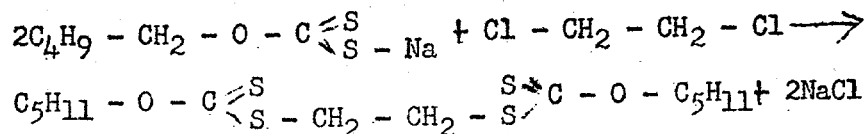
However, an extreme pressure agent should be "corrosive", forming metal compounds, only under the conditions of extreme load. Therefore, an agent should be chosen which is non-corrosive at low temperatures but which becomes suddenly corrosive at some elevated temperature. With such an agent, those spots or areas which become warm from friction will be attacked by the agent, forming a metal compound which will provide the "lubrication" necessary to prevent overheating and seizure.

One compound prepared by I. G. - Leuna possesses such a temperature-corrosivity relationship and was used as an ingredient of their extreme pressure lubricants. The compound, known as Mesulphol, was synthesized as follows:

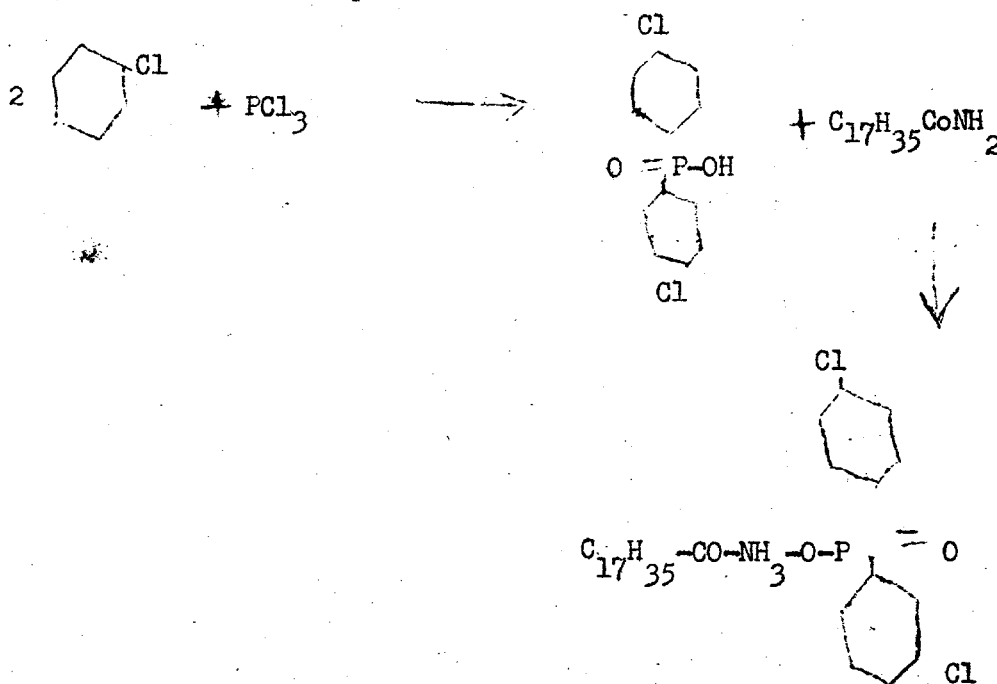


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10. Additives to Lubricating Oils, (c) (Cont'd.)



A new compound was being manufactured by I.G. Leuerkusen for use as an ingredient of aeroplane engine break-in oils. The agent is a phosphorous compound manufactured from chlorbenzene phosphorus trichloride and stearyl amine. The use of 0.5 to 1.0 percent weight of this compound in oil reduced the break-in time for aeroplane engines from 50 hours to 10 hours. It had been in small production at Leuerkusen since 1943, the total output having gone to Daimler-Benz and Junkers for the above use. The compound was prepared as follows:



Details on the manufacture of this compound will be found in U. S. Naval Technical Mission in Europe Letter Report No. 119-45 (s) of 12 June 1945.

In Germany, testing of extreme pressure lubricants and additives was carried out with various test devices. The four-ball machine was used, but was not regarded as a good device. The Alman-Wieland test

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10. Additives to Lubricating Oils, (c) (Cont'd.)

machine was also used. A test apparatus recently developed consisted of a slowly revolving metal drum, partly immersed in oil, with a metal wire under tension in contact with 180 degrees of the drum. The wire is put under such tension that the area of contact is under very high load. The friction drag is measured by the difference in tension between the two (2) ends of the wire. This machine then measures friction against speed of rotation at constant temperature, or against temperature at constant speed.

(d) Pour Point Depressors:

Paraflow was being manufactured in Germany. The process consisted of condensing 80 parts of chlorinated paraffin with 15 parts of naphthalene and one part of polystyrene, using $AlCl_3$ as a catalyst and a temperature of 85 degrees fahrenheit. The polystyrene inclusion was said to "double the effect" of the Paraflow addition to lubricating oils. In 1942, about 10,000 barrels of Paraflow was manufactured and sold in a concentrate containing 8 percent Paraflow and 92 percent oil.

(e) Viscosity Index Enhancers:

Polyisobutylene was being manufactured and sold in Germany under the trade name of Oppanol (I. G. - Oppau). Its use was limited to the increase of VI of a few low grade lubricating oils to make them salable as motor oils.

(f) The Principle of Two-Phase Lubricants.

It is perhaps worthwhile to mention that work was in progress in one research laboratory on a two-phase lubricating liquid. The goal was the supply to the engine or device a lubricating medium that would not change viscosity with temperature. The principle was to use a two-phase system, wherein phase A is a lubricant and phase B is a more viscous liquid, with or without lubricant properties. As temperature increases the solubility of phase B in phase A increases at such a rate that the viscosity of phase A remains constant. No commercial application of the principle has been made or have, in fact, specific phase compositions of such a system been worked out.

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11. Lubricating Greases:

Very few new developments in grease manufacture or use were found. The components of greases are no different from those that are in conventional use in America

Soaps for grease manufacture were made largely from synthetic fatty acids. These fatty acids were made by the Deutsche Fettsaure Werke (Witten), I. G. (Oppau and Heydebrek), and a plant in Magdeburg by oxidizing normal paraffins from waxes. The total fatty acid production for this use was about 120,000 tons per year. The soaps used in greases were primarily sodium, calcium, and aluminum. The use of Lithium soaps for greases was known and a very small volume was being produced, but there was apparently only little interest in and no plans for extended use of them.

The oil components of German greases were almost exclusively refined petroleum fractions and, most commonly, of Pennsylvania origin. No important use had been made of the synthetic lubricating oils produced in Germany as grease components.

One development that was found was the use of finely divided silicon dioxide to produce gels with lubricating oils. It was a development by the Degussa Company (Deutsche Gold und Silber Scheide-Anstalt). The finely divided SiO_2 is prepared by burning silicon tetrachloride and directing the flame against a cooled metal surface. The silica product has a particle size distribution similar to that of carbon black and a settled density of only 0.015. Used in 5 to 10 percent concentration with certain lubricating oils, particularly those containing an appreciable content of polar compounds, a stable gel was set up which could be used as a grease. The gels were said to be stable over a temperature range of -65 to +570 degrees fahrenheit.

The following document, transmitted to the Bureau of Ships, pertains to German lubricating greases:

XIV Technische Lieferbedingungen fur Flieger-Sonderfette. (Specifications for greases supplied to the German Air Ministry).

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12 Conclusions.

(a) The total volume of lubricating oils produced for German use during the last war years was about 17,500 barrels per day. Of this total, only 1,700 barrels per day came from synthetic processes and the remainder was obtained from petroleum.

(b) The refining methods employed to obtain finished lubricating oils from petroleum were largely conventional and are well known in America. A new process not yet applied commercially was known as Mixed-Polymerization. It involves the addition of ethylene and its polymers to petroleum lubricating oil distillates as a refining process, thereby obviating the necessity of solvent extraction.

(c) The synthetic oils came from the following processes and locations:

(1) The TTH process at Brabag-Zeitz produced 600 barrels per day of industrial quality lubricating oil. This process hydrogenates brown coal tar under such conditions that a lubricating oil fraction of average quality only is obtained directly as a main product.

(2) At I. G. Leuna polymerization of ethylene to produce high quality oils was being carried out. Using a new process of I. G. origin, oils of 120 VI, low pour point, and good stability in use, were being made. These oils, produced at a rate of 300 barrels per day, were being used in 50/50 admixture with refined petroleum fractions as 100 VI aircraft oils.

(3) At Ruhrchemie-Halten, Rhenania Desag-Hamburg, and Politz, olefins produced by thermal cracking of high boiling paraffins were polymerized to high quality oils of 110 to 120 VI. Of these oils, produced at a combined rate of 650 barrels per day, most were used with refined petroleum fractions to produce aircraft oils.

(4) Using a process of their own development, Rheinpreussen-Homburg produced 50 barrels per day of oils by alkylating a naphthalene with a C_{16} paraffinic chain. Their production was taken entirely by the German Navy for use in diesel engines.

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12 Conclusions (Cont'd.)

(d) Several esters were being synthesized by I. G. - Leuna for use as components in special oils requiring low pour points and high VI. Esters impart good lubricating quality ("oiliness") to a mixture, at the same time fulfilling other requirements of a good lubricant. The VI of esters are 150 to 250, and their pour points are about -40 degrees fahrenheit. The ester development is considered to be of outstanding interest. The I.G.- Leuna ester production rate was 100 barrels per day.

(e) Synthetic oils developed, but not produced commercially, included a polymer of tetrahydrofuran and ethylene oxide (I.G.- Leverkusen), and a water-soluble salt of triethanol amine and a ca. C₈ fatty acid (Deutsche Fettsaure Werke-Witten). The former compound has a high VI and low pour point, but little information is available on its performance. The water-soluble oil was developed for torpedo use and was said to have been accepted by the German Navy.

(f) Several new additives had been developed, including an oxidation inhibitor (an organic tin compound), a corrosion inhibitor especially effective on iron, and two (2) extreme pressure compounds.

(g) No outstanding new developments in the field of lubricating greases were found.

(h) Of the new synthetic oils and components disclosed, the polyethylene oil and the ester additives are considered to be of particular interest and their study and test by the U.S. Navy is recommended. The new additives described should also be tested by methods in standard use in America.

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APPENDIX I.

THE MANUFACTURE OF ETHYLENE FROM ETHANE

Ethylene for the manufacture of ethylene polymer lubricating oils was produced at Leuna by the partial oxidation of ethane.

The Leuna process gives an ethylene yield in the plant of 70 percent weight, based on charged ethane. The ethane to be reacted is three (3) volumes is heated to 1110 percent weight, oxygen one volume is separately preheated to 750 degrees fahrenheit, and the two are combined under slight vacuum in a carefully designed burner wherein the temperature rises to 1470 to 1560 degrees fahrenheit. The product of the furnace is cooled by exchange and the ethylene is separated and purified to a minimum of 95 percent weight, in the final product.

On a hydrogen and nitrogen free basis, the product from the reaction burner is:

48.1 percent vol.	Ethylene
30.5 percent vol.	Ethane
16.0 percent vol.	CO
0.6 percent vol.	CO ₂
1.6 percent vol.	O ₂
2.4 percent vol.	Propylene and Higher Olefins
0.8 percent vol.	Acetylene
<hr/> 100.0	

Based on ethane recycle to extinction, the above analysis corresponds to an ultimate ethylene yield of 79 percent. This figure is reduced, of course, by losses in the recovery and separation system

The ethylene was purified at Leuna by a Linde fractionation system. Before fractionation, CO₂ was removed with an alkazid plant (regenerative alpha-amino-propionic acid) and acetylene was hydrogenated over a nickel-chrome catalyst down to a content of 0.1 percent volume. The first Linde column separated overhead materials lighter than C₂, a second column separated the

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Appendix I (Cont'd.)

C₂ fraction overhead, and a third column separated ethane and ethylene. Through this fractionation, CO was also separated quite completely from the ethylene.

A second method for ethylene manufacture from ethane was worked out at Leuna and a plant was being built at Heydebrek. The dehydrogenation step in this system employs straight thermal cracking at atmospheric pressure. In a two stage counterflow of flue gas and ethane feed through two furnaces, the ethane temperature is raised to 1200 degrees fahrenheit in the first coil and to 1550 degrees fahrenheit in the second. The cracked gas is quenched, acetylene is selectively hydrogenated out, and the gas passes to a selective solvent ethylene concentration system.

In the thermal cracking operation, a conversion of 30 percent per pass is obtained (design figure for Heydebrek). In pilot plant work, coke deposition in the 27 percent chrome tubes required a cleanout only once in 40 days.

With a thermal cracking method for the ethane dehydrogenation, a system of selective absorption was to be used for ethylene recovery. The solvent is a copper - diethanol amine complex, prepared by saturating diethanol amine with cuprous nitrate and adding thereto 3 to 4 percent weight of ammonia water. This solvent is used at 80 degrees fahrenheit and under 10 to 20 atmospheres pressure. Ethylene is released by reducing pressure and increasing temperature to 105 degrees fahrenheit.

When recovering ethylene from a 30 percent concentration gas mixture, one volume of solvent at 15 atmospheres is adequate to scrub 30 volumes of gas down to an ethylene content of 0.2 percent volume.

This solvent will separate ethylene from paraffins but is not selective between ethylene and propylene. It will not separate CO from ethylene, and hence is not used when ethylene is produced by partial combustion of ethane. Sulfur compounds in a gas being treated with this solvent react with the solution and precipitate copper sulfide which then must be filtered out periodically. If CO is to be separated, Linde fractionation is considered to be the most practical method. Removal of CO with a KNi CN₂ solution had been studied, but the process is not

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Appendix I (Cont'd.)

regenerative and hence is costly for high CO concentrations.

The following documents transmitted to the Bureau of Ships, pertain to the manufacture and concentration of ethylene by the two systems outlined:

- XV Die Herstellung lines Athylenhaltigen Gases durch thermische Spaltung von Althan oder Propan und Aufarbeitung dieses Spaltgases auf Reinathylen in einer Gastrennanlage nach Linde. (I. G. Leuna - Report).
- XVI Gestehkostenvorausschätzung für Athylen aus Athan durch thermische Spaltung im Rohrenofen nach Hauber. (I.G. - Leuna - Bericht of 11 June 1941)
- XVII Schema zur Spaltanlage. (I. G. - Leuna - Flow diagram of Ethane Thermal Cracking Unit-20 April 1943).
- XVIII Olefinabsorption mittels Cuprosalzlosungen II Mitteilung. (I. G. - Leuna - Dr. Hauber report of 22 July 1942)

*The above enclosures appear on T.O.M.
Reel 135.*