

Memo dated 19.4.44

The replacement of "Kogasin" by other basic materials for Sulfo-chlorination - report for the "Wero" experts' conference
28.3.1944.

Generally speaking Kogasin has proved to be a very good initial substance for Sulfo-chlorination. Its cost-price, however, is relatively high, for it is chemically very homogeneous, pure, synthetic paraffin oil. Its production depends also upon the number of existing "Fischer" plants, thus limiting the quantity at our disposal. Finally one must not forget the Government's control of raw materials which enable the authorities to direct the distribution of Kogasin according to the actual situation of these raw materials. Therefore an attempt was very soon made to substitute other cheap and easily available commercial oils for the Kogasin. A mineral oil product was obviously indicated for this purpose. If the production of capillary active substances is also aimed at, one should first of all turn to the mineral-oil distillates used for Diesel oils. Director Dr. HEROLD spoke already briefly in the "Wero" session of February 2nd, 1943 about the possibilities of substituting mineral oil products for Kogasin II in order to produce "Mersolate". Therefore a short summary is here repeated of the results before dealing with the more recent experiments.

It is not possible to sulfo-chlorinate mineral oils if they are not treated beforehand, but Kogasin II can in principle be sulfo-chlorinated without any preliminary treatment though, because of the chlorine addition to the olefinic bonds, the final product contains more chain chlorine compounds than the sulfo-chlorinated "Mepasin". In the case of paraffinic mineral oil distillates it is sufficient to use the conventional mild hydrogenation as a preliminary treatment for the sulfo-chlorination which is carried out at a temperature of approximately 380°, a temperature which is higher by about 50° compared with the Kogasin. Nickel tungsten sulfide is present as a catalyst. The oils which are then obtained can be sulfo-chlorinated, though a higher content of chain chlorine compounds can always be noticed in the final product when compared with the Mersols obtained from Kogasin. When high density mineral oils are used, a large proportion of which will be readily absorbed in sulfuric acid, we recommend strongly treating these oils before the hydrogenation with liquid SO₂ or with another solvent of greater catalytic efficiency. This will diminish the content of cyclic compounds in the oil which facilitate the formation of chain chlorine compounds. Such oil can in principle be sulfo-chlorinated after hydrogenation, though the reaction is somewhat slower in comparison to Mepasin and though the content of chain chlorine compounds is a little higher. The following table shows the difference when the various basic oils are transformed to Mersol:

Table I

Product	Duration of sulfo-chlorination	Hydrolyseable chlorine	Chain chlorine compounds	Density
Rumsåden paraffinic oil pre-extracted and hydrogenated. 240-320°	11 hours	5.2	1.3	0.801
Mepasin	8 hours	5.3	0.8	0.776

There was no difficulty in saponifying the Mersols obtained from the middle oils to Mersolates. The colour of the Mersolates, however, is often unsatisfactory. Whilst Mersolates on a basis of Kogasin are colourless or slightly yellow, those on a mineral oil basis show colours varying from yellow to chocolate-brown. The colour is more intensive in those cases where more cyclic compounds are found in the basic oil, particularly such with condensed ring-systems, e.g. of the Decalin type. Therefore colourless

or only faintly coloured mineral oil Mercosolates are only obtained from mineral oils which either originally contain only a low proportion of cyclic hydrocarbons or from which a large proportion of these undesirable cyclic constituents have been extracted by means of a pre-treatment with solvents. Great progress was made in the production of light mineral oil-sulphonates by adding a little sodium hydrosulphide to the saponifying solution before vaporizing. But the greatest problem in the production of mineral oil Mercosolates consists in restoring the recycle oils which are given off during the saponification of Mercosol H. They can again be sulfo-chlorinated without further preliminary treatment in the case of Mepasin, but mineral oil products must at first be hydrogenated in order to eliminate the substances which would inhibit the sulfo-chlorination. This hydrogenation itself runs smoothly, but it involves problems of corrosion because the recycle oils contain chlorine. These corrosion problems appear to have been solved in laboratory tests, but need confirmation by tests on a large scale.

An extensive use has recently been made of Mercosol H in which the hydrocarbons accompanying the sulfo-chloride do not appear as a recycle oil after the conversion but remain in the final product. These are the Höchst drilling oils which are produced by converting the Mercosol H into the corresponding sulfonide - the Neulsol H - and by the further action of chloroacetic acid on the sodium compound of the Neulsol H. The effective substance of the drilling oils is the sodium salt of the sulfo-amido-acetic acid of Mepasin. But the presence of hydrocarbon oils is also necessary. This is in fact the case, since Mercosol H carries approximately 50 to 55% hydrocarbons. The whole process necessary with recycle oils is thus eliminated when producing drilling oils, and therefore the use of other oils instead of Mepasin commands itself very strongly for the production of Mercosol which we used for making drilling oils.

The drilling oils hitherto usually manufactured for the metal engineering industry were on the basis of spindle oil. Since the Höchst drilling oils should be substitutes for these products, it was obvious that the Government placed spindle oils at our disposal. But some difficulties were met when using these oils. The hydrogenation had to be carried out first of all by means of the spray process. The yields, however, were quite small considering the time and space needed. Secondly it was not possible to sulfo-chlorinate the oils smoothly. This was particularly true for oils obtained by means of relatively mild hydrogenation at 330° preserving as much as possible the molecular size of the hydrocarbons. These oils proved to be very unsatisfactory for sulfo-chlorination. Firstly it was found that the sulfo-chlorination was very slow, and secondly, it was found that considerable quantities of chain chlorine compounds were formed. This was very undesirable. These products can therefore not be used for the manufacture of drilling oil because of the danger of corrosion caused by the liberation of halogen. We even observed the formation of notable quantities of sulfuryl chloride during the sulfo-chlorination of the spindle oils which were treated preliminarily in this way. Thus such products should not be used for sulfo-chlorination. The results were better when hydrogenation of the spindle oils was carried out at higher temperatures. But then it was found that the hydrocarbon molecules cracked in part and that these products had boiling points up to the range of the boiling point of gasoline. Generally hydrogenation was carried out in such a way as to obtain products containing not more than 20% constituents boiling below 200°. After distilling the constituents which boiled below 200° and perhaps bleaching the residue; this residue could be sulfo-chlorinated with greater speed, but it was even more important that the quantity of chain chlorine compounds was considerably less. By the intensive treatment with hydrogen the original oil has obviously been freed from the substances inhibiting the sulfo-chlorination (chain inhibitors). But the values for chain chlorine compounds are still far above those which were found for Mepasin

Table 2

Product	Hydrolysable chlorine	chain chlorine compounds
Mepasin	5.3	0.8
Spindle oil hydrogenated at 340°	6.0	7.2
Spindle oil hydrogenated at 330°	5.6	2.0
Paraffin, Rumanian Mineral oil	5.2	1.3

In spite of these facts Mersol H products were obtained in many cases, particularly from spindle oils from Dollbergen, and the Höchst works considered these Mersol H products suitable for the manufacture of drilling oil. Unfortunately the Government permit for this kind of spindle oil was unobtainable. All types of spindle oil released by the Government were subject to a preliminary treatment involving hydrogenation and cracking. The products of this preliminary treatment were ill-suited for the manufacture of Mersol H used in drilling oil factories. This means that spindle oil cannot be considered at present as a substitute for Kogasin for the purpose of drilling oil production on a Mepsin sulfonate basis. The end of the tests showed that a cracking hydrogenated spindle oil of low viscosity of Tesaro, Brabag Zeitz was nearly as good as the oils from Dollbergen. Some of the Diesel fuels of Austrian and Polish origin were released by the Government but proved also to be unsuitable for the manufacture of Mersol H, since they formed too many chain chlorine compounds after hydrogenation. Oils of this type can probably only be used for the production of Mersol H if they are pre-treated with liquid sulphur dioxide before subjecting them to hydrogenation. Thus a Hungarian gas-oil was treated by extraction with liquid SO₂, and after hydrogenation a saturated oil was obtained with a density of 0.807. When sulfo-chlorinated a Mersol H with 5.3 hydrolysable chlorine and with 1.3% chain chlorine compounds was obtained, which means that this product was similar to the product which was obtained already from a highly paraffinic hydrogenated Rumanian gas-oil well suited for the manufacture of drilling oils. The Government, however, refused to release highly paraffinic Rumanian gas-oils for the manufacture of drilling-oils. Other gas oils with a larger quantity of cyclic compounds could not be used, because no suitable "Edeleanu" plants were available and these plants are needed for the SO₂ extraction.

Some time ago two other industrial special products were tested as to their suitability for sulfo-chlorination. These are the first runnings of crude paraffin by Zeitz and the first runnings of lubricating oil by Pöhlitz.

The first product is formed when hydrogenating the Zeitz crude paraffin, because it has to be pre-treated by hydrogenation for the purpose of oxidation of the paraffin. This leads necessarily to a cracking, forming products of a lower molecular weight. When the fraction 230-320° is distilled off from the first running constituting approximately half of this first running, and when it is then carefully hydrogenated again at 320°, a saturated oil is obtained with the density 0.808 which is suitable for Mersol H production. The result is a Mersol H with 5.5% hydrolysable chlorine and 1.4% chain chlorine compounds. The product is in Höchst to be tested. The data show that it is probably suitable for the manufacture of drilling oils.

The other oil is formed by the cracking of hard paraffin, and the resulting olefins were then polymerised with AlCl₃. Thus a first running of lubricating oils is obtained. Its boiling point is within the range of 250-350° at a density of 0.792. It is easily hydrogenated. The density drops to 0.785 during this process without altering the boiling curve very much. This shows that it is a highly paraffinic product. The sulfo-chlorination gives in fact a Mersol H with 5.0% hydrolysable chlorine and 0.9% chain chlorine compounds, i.e. a product with approximately the same qualities as those which were obtained on a Kogasin basis. This Mersol H also is in Höchst for testing. The analytic data of this Mersol indicate that it will also be suitable for the drilling oil production. 100 tons per month would be available if the Government were to release these two oils which were just described, so that a planned development of the drilling oil production to a total of 700 tons per month would relieve to a certain extent the demands on Kogasin.

(signed) Smeykal

Mersol and its derivatives

Kogasino

Mepasino

Mersol

Mersol D

Mersolate D

Mersol (H₂SO)

Ca-, Mg-
Mersolate - IC Mersolate
antifoamer

insecticide

emulsifiers,
cosmetics, pharmaceutical

industrial cleansing agents

Sulfanido

Phenyl-Est

Mazemoll

Softener

Tanning material
"Lumergan"

Raw materials
for detergents

Emulsifier for
synthetic materials

Essic material
for textile processing

Derminol
liquor

Emulsifier
for drilling-oil

hair and hand
washing
material

sosp
cakes

washing
powder

washing-
pastes

wetting
agent

dispersing
agent

wool- and fur-
washing material

greasing
agent

Possibilities for the uses of Mercal or Mercolate
as washing materials

A) Toilet

	<u>Tons per year, Mercolat 100%</u>	
Standard Fancy Toilet Soap	12,000	
Shaving Soap	4,160	
Shampoos	490	
Toothpastes	160	16,810

B) Washing Material

Washing powder	30,000	
Washing soap (curd soap)	4,400	
MS soap	5,800	
Fine washing material	2,900	
Cleansing material of all kinds	4,800	47,900

Total Mercolat 54,710

Required quantity of Kogasin	45,000 tons
"Rif" quantities for 1944	38,300 tons
Kogasin for non-acap Mercal (and other purposes)	14,000 tons

Uses of Mersol
 apart from washing materials
1943

	Tons per year	
	Mersol or Mersolat of 100%	Manufactured products
Messnoll	2358	3818
Drilling oils (Höchst)	1000	2300
Emulsifier for synthetic materials	636	900
Liquor oils (Licker-Öl)	450	1640
Processing materials for textiles	250	301
Industrial cleansing materials	300	900
Anti-foamer	173	480
Tanning material Immergen	90	110
Insecticide	75	1750