Standard Oil Company
(Indiana)

INFORMATION DIVISION TRANSLATION T46-73

API-TOM Reel 79, Frames 2252-2275
Ammonium Works, Merseberg, April 24, 1944
Concerning: Processing of Aluminum Chloride Sludge*
To North German Mineral Works G.m.b.H.

Replying to your letter to our Dr. Zorn concerning corrosion resistant pumps and fittings for processing of your aluminum chloride-containing sludge, we would like to let you know that according to our experience the use of normal cast iron pumps and fittings is entirely possible. We too had originally iron pumps in operation and we still have normal fittings built in. Until the Fesi pumps which you have ordered are delivered you can use without further ado your available iron pumps with similar pressure and conveying capacity.

You may be interested that the processes that we have reported to you did not cause any trouble or changes in the meanwhile.

Aluminum Chloride

Aluminum chloride must be treated with particular care because of its sensitivity against water and moist air. Upon action of moisture there are formed hydrochloric vapors which corrode metal, particularly iron. Numerous experiments carried out in Oppau disclosed that a thin oil layer is formed in the stirring containers, on the walls in the heating and cooling plants providing a good protection. Such thin oil layers occur in the operation of polymerization and decomposition vessels. Further it needs to be observed that the inhaling of hydrochloric acid vapors which are formed in the moist air is kept in very small amounts. Very small amounts are already found to be annoying, larger amounts of vapors are very disturbing and can under circumstances harm the health and can cause severe bronchial catarrhs.

Daily requirements of $AlCl_3$ approximately 3 tonnes.

Weekly requirements of $AlCl_3$ about 20 tonnes or about 20 cu.meters.

A. Transportation and Transfer

Originally small 60 kg. cans with special closing devices were used for the transport from Ludwigshafen to Pölitz. These cans were chosen because their contents correspond exactly to one charge that is used in the polymerization. It seems these cans were too sensitive. In the first transport of 250 pieces 28 cans were damaged, in the second 14. The first transport was by water, the second by railway. Therefore, it seems practical that the transport from Ludwigshafen is done in stable original containers.

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* A series of letters forming a continued correspondence file on the subject.

These can be filled over into small cans at Politz.

The original containers that arrive are opened in a room which is provided with some ventilation to eliminate the hydrochloric acid vapors that may form in there. This room is on the first floor of building 744. Then they are tilted by a special trucking installation into an acid-fast masonry or concrete bunker which is in the basement. The take-out opening in the bunker is so high that one can easily put a can under it. One can connect a can most dust-tight by a soft connection. The tipping over occurs in a closed bunker by pushing the opened barrel into a cage which can be turned according to its horizontal axis and it is constructed in such a manner that the falling out of the tilted barrel is impossible. Another construction may possibly be more practical. The soft connection between bunker and can can be made of leather, rubber or solid material. It is fastened firmly at one end to the bunker and on the other it has a closing device which can be set on the special closing device on the can. The cans are filled up to almost the top and then the net weight is determined.

This manner of operation seems more practical than that which was planned originally. In the original plan the tilting over of the barrels was planned in an open room by a tilter that could be turned.

B. Aluminum Chloride-Containing Sludge

The aluminum chloride-containing sludge is just as sensitive to moisture as $AlCl_3$ proper. This sensitivity can cause the same difficulties as those described above for aluminum chloride. It may cause corrosion or harmful action on the breathing organs. Also, upon contact of larger amounts of water may cause solid depositions which may cause disturbances in the piping and pumps.

One therefore has to watch that the sludge should be as little in contact with air as possible. This is done by the collecting containers in Building 744 most practically by putting the sludge which is stored there constantly under a layer of oil which is not too small. The piping for the sludge must in no case consist of double jacket metal pipes. Heating which may be necessary in order to make the sludge more easy to pump must only be done through welded steam pipes.

The entrance opening of the pipe in the storage container or in the decomposition kettle should lie deep under a long vertical piece of pipe, which has a cap on the top through which one could eliminate possible obstruction through pushing with a long bar. Upon decomposition of the sludge with little water first the necessary amount of diluent should be put into the decomposition kettle, then, only, the sludge. The oil which is formed in this decomposition should be washed with (blank)% sodium hydroxide, which can be used several times.

C. Oil-Containing Clay

The oil-containing clay which is taken out from the slide centrifuge is corrected in a bunker, whose walls are made of iron. The clay is put into an empty aluminum chloride drum through a opening at the bottom which can be closed. The drums are closed according to the directions and taken to the loading platform by means of an electric cart.

(Stettin-Pölitz , July 21, 1944)

Corrosion Tests

Aqueous aluminum chloride solution against iron sheet metal

Surface of the sheet metal strips about 15 sq. centimeters, Temperature 20°C.

From experimental series #1

Table I

Experimental Series 1

$AlCl_3$ in H_2O, concentration of the solution	Duration	Weight		Loss	
		before g	after g	G/sq.M. in 24 hrs.	Layer thickness per year
26.4%	18 hrs.	5.7879	5.7855	2.2	0.1 mm
41.6%	18 hrs.	5.4179	5.4158	2.0	0.09 "
for comparison, normal HCl	18 hrs.	5.6851	4.4724	1038	50.0

The attack upon iron decreases after some time. Apparently a protective layer is formed.

Experimental Series 2

Loss after hrs. total	Difference from the previous observation in hours	Weight decrease in grams	
		in 26.4%	in 41.6%
1	—	0.0025	0.0028
2	1	0.0006	0.0008
4	2	0.0005	0.0005
6	2	0.0005	0.0002
20	14	0.0009	0.0007
44	24	0.0015	0.0006
68	24	0.0025	0.0010
92	24	0.0025	0.0010

Experimental Series 3

The attack numbers for 2 strips of sheet metal that were welded together are as follows:

Loss after hours inclusive	Difference from the previous observations in hours	Weight decrease in grams 35.6% solution
1	—	0.0071
2	1	0.0014
3	1	0.0006
4	1	0.0004
5	1	0.0004
40	35	0.0026

Zinc sheet metal strips were completely dissolved in a very short time. One must observe when one evaluates the results of the experiment that the experiments were carried out with filtered clear aluminum chloride solution. As you know the solution that results in our operation contains a certain amount of oil. It probably deposits partially on the wall and influences the corrosion favorably.

(Frame 2258) German Vacuum Oil Co. Office Dr. Pfefferkorn in Aumühle near Hamburg - January 22, 1944.
Concerning utilization of aluminum chloride sludge. Letter of DVOAG from Dec. 23, 1943, Dr. Pf La

According to your request we shall once again discuss your letter of Dec. 23, 1943.

First, we state that two different phases must be considered in order to evaluate the question.

1) The present situation in which oil-containing aluminum chloride sludge is formed which cannot be delivered in its entirety to I.G. as was planned originally, because there are difficulties in processing or marketing from time to time.

2) Also, we must consider the sludge that will be formed upon execution of the changes which are planned. The oil that is contained in the sludge will remain in the plant while the aqueous solution will be delivered to I.G.

To the various points we note as follows:

1. We are also of the opinion that it is our most urgent task to reduce the operation losses which still exist at present. Until the beginning of 1943 the technical solution of another possibility of processing for the aluminum chloride sludge which was formed was not known. From the beginning of the production we have tried and as soon as the necessary practices were known we have introduced them.

2) As you can see from our previous remarks and from our letter from Dec. 29, 1943, we hope that we shall be able to carry out the sludge decomposition ourselves. Therefore, the main problem is to market the aluminum chloride sludge which is stored up here at present. We had planned to process also these quantities in our new processing method. But we would like to try to get rid of that stock as soon as possible.

3) We doubt whether it shall be possible to find a customer who is willing to pay 2 reichsmarks per 100 kilograms of the aluminum chloride sludge. On the other hand, we shall hardly be able to recover the total amount of oily components. But even if we recover 15% of the oil from 2,400 tonnes of sludge per year, which equals about 350 tonnes of oil at the price of 100 reichsmarks per 100 kilograms there results a value of 350,000 reichsmarks.

4) As we have said repeatedly we shall undertake the sludge decomposition ourselves. The necessary masonry of a tank will be started in the next few days and we hope at the beginning of April of this year the preparatory work will be completed.

a) The method is known and will be undertaken. A cylinder oil is formed with a flash point of 310-320°C, a viscosity of 60 centistokes at 100°, Conradson 1.46%.

b) See our letter of Dec. 29, 1943. It will probably cost about RM-13,500.

5) The concentrated aqueous solution of aluminum chloride is to be delivered in special transport vessels to I.G. Ludwigshafen. In case that I.G. does not accept this solution it will be difficult to add it to the waste water.

As we have already indicated we condider it possible to decompose the amounts of sludge that cannot be disposed of. But we would like to remove them from our premises. There are about 250 tonnes of sludge here. The transport can be done either in lime cars or 200 open freight cars by the state railroad. The sludge contains about 17% of oil and 83% of aluminum chloride hydrate.

We hope that we have given you now sufficient information about these prevailing questions, and again remark that I.G. takes again at present 10 cars per month.

/s/ North German Mineral Oil Works at Stettin

(Frame 2260) Hamburg Jan. 7, 1944, Notice - Dr. Bieler

NNW Utilization of Aluminum Chloride Sludge

About the subject "Utilization of aluminum chloride sludge" we have three letters from NNW Pölitz (letters of 7, 17 and 29 of Dec. 1943), and the opinion of DVOAG of Dec. 23, 1943. The latter starts out from the yield review of the month November 1943. They found out that the total operation losses which have been shown of 8.68%, and of 5.80% from the polymerization are unbearable industrially. Also, the filtering loss which is given at 1.22% is considered very high.

It is obvious that the losses which occur in each processing must be reduced so far as it can be carried out technically and economically. It is the opinion of DVOAG that the total loss as it is formed in the polymerization and the partial loss in the filtration is too high. However, it should be practical not to use the operation month November 1943 in the treatment of the loss problem, since it was not free of operation disturbances. But in order to eliminate as much as possible the chances of monthly fluctuation, it should be based on a longer period of time. I point out my letter to you of Dec. 20, 1943, to which I added a summary of the processing of the three months September to November 1943. Here the following losses were obtained in the processing of 100% paraffins.

Cracking	0.66%
Polymerization	5.77%
Distillation of crude thick oil	0.29%
Distillation of crude cylinder oil	0.19%
Filtration of thick oil	1.19%
Total losses	8.10%

Also according to this the partial losses in polymerization and filtration are very high and deviate in general only little from the proven partial losses for November.

The most urgent task in this connection is without doubt the reduction of the losses in the polymerization. It seems obvious to think thereby primarily on the processing of the aluminum chloride sludge which is formed in the polymerization. But it seems noteworthy that the NNW has apprently not come to a unified opinion about the utilization of aluminum chloride sludge. On Dec. 17, 1943 they seemed to consider it very important to get rid of the aluminum chloride sludge without pay, and with renouncing claims to return shipments of oil. On Dec. 29, 12 days later, a processing method which is to be operated in short time is represented in its basic points.

It seems worth knowing how much the loss of polymerization can be reduced in the most favorable case in the processing of the aluminum chloride sludge and how much the oil yield can be increased. According to the letter of NMW of Dec. 7, 1943 the aluminum chloride sludge consists on the average of 80% to 83% aluminum chloride hydrate ($AlCl_3.6H_2O$) and 17-20% of oil. For the calculations of the utilization of the sludge is to be assumed the most favorable composition, therefore 80% aluminum chloride hydrate and 20% of oil.

In the three months September to November 1943, 5,400,528 kgs. liquid olefins (equals 71.53% calculated on paraffin), 372,862 kgs. of water-free aluminum chloride (6.90% calculated on olefins) or 4.94% calculated on paraffins was used in the polymerization. 4.94% water-free aluminum chloride corresponds to $\frac{4.94 \times 241.44}{133.34}$ = 8.94% aluminum chloride hydrate, or since the aluminum chloride hydrate is contained in the aluminum chloride sludge up to 80%, it amounts to 11.18% aluminum chloride sludge. In other words, at the most 11.18 minus 8.94 = 2.24% oil is the maximum that can be recovered through processing of the aluminum chloride sludge, calculated on 100% paraffin according to the analysis of NMW. Thus, the polymerization loss would be reduced from 5.77% to 3.53%. This result cannot satisfy because a polymerization loss of 3.53% after recovery of the oil from the aluminum chloride sludge requires a clarification of the cause of its formation and a reduction to a tolerable over-all dimension.

The processing procedure which is sketched in the letter of NMW for the aluminum chloride sludge should not cause any difficulties concerning the separation of the oil and the aluminum chloride solution so far as we can see. But it would have been interesting to find out what proceeds one can expect from the I.G. for the aluminum chloride solution. It would depend upon this question whether the processing of the sludge as planned would be economical or not. One has to reckon with high costs because of the strongly corrosive action of the aluminum chloride solution so far as the operating is concerned. This includes both construction as well as operation costs. The aluminum chloride sludge utilization which is planned by NMW in the letter of Dec. 29, 1943, still needs a careful testing so far as apparatus and economy is concerned, not so far as the operation is concerned. If I.G. is so much interested in the aluminum chloride solution then it may be advantageous for NMW to sell this sludge against a price to I.G. instead of procuring their old processing installations.

(Frame 2262) Remark - Dr. Bieler, Hamburg January 7, 1944

NMW Filtration Loss

In the letter of DVOAG of Dec. 23, 1943, which had the title "Aluminum Chloride Sludge Utilization", the filtration loss which was given at 1.22% for the month of November 1943 was considered very high and according to my opinion, this is justified.

The filtration loss which was obtained in the operation for the three months September to November, 1943 (compare my letter and appendix of Dec. 20, 1943) amounted to 2.59% calculated on unfiltered thick oil, respectively 1.19% calculated on paraffin. If one wants to test the magnitude of filtration loss with regard whether it is justified or not, one starts out most practically from the bleaching earth which was used for the refining of the unfiltered thick oil. It is known that in trouble-free operation of the filter press work one obtains a bleaching earth residue which consists 2/3 of bleaching earth and 1/3 of oil. Thus the filtration loss should be only half as much as the bleaching earth used. So far, one foregoes the recovery of the oil from the bleaching earth residues because of the usual poor quality of the oil which is absorbed on bleaching earth.

One used 3,256,285 kgs. of unfiltered thick oil (45.89% calculated on paraffin, and 39,325 kgs. bleaching earth which equals 1.20% calculated on thick oil in the operation for the three months. Upon careful filter press operation the filter loss should not be more than 0.60% calculated on unfiltered thick oil or 0.28% calculated on paraffin. If one makes less stringent requirements for the filter press operation than this, which is practically obtainable, the filter loss may be as high as the bleaching earth amount. In the highest case the filtration loss is for three months September to November 1943, calculated on unfiltered thick oil, should be 1.20% and calculated on paraffin 0.55%.

Thus, it appears that the filtering loss could be reduced to half without processing the bleaching earth residues whose success is questionable.

(Frame 2263) German Vacuum Oil Co.: Attention: Dr. Pfefferkorn, Aumühle,
near Hamburg, Dec. 29, 1943.

Aluminum Chloride Sludge Utilization

Already in January 1943 we decided to process the aluminum chloride-containing sludge by another method than the one used now. This process is changed somewhat from that which we used sometime ago at Oppau. These changes had been worked out in Leuna and carried out there. They consist in the fact that the sludge is brought together with water in a nozzle under pressure after separating from the crude thick oil. Aqueous and oily layers are formed which are separated from one another and the water in which aluminum chloride has been accumulated is used several times for new reactions. In this manner one obtains highly concentrated solutions of aluminum chloride in water which I.G. in Ludwigshafen seem to be very interested in. They produced textile auxiliary agents from this solution. We have included this point in the budget for the year 1943 under #19 and again for 1944 under #13.

Since the aluminum chloride-containing solution is very corrosive the portions of the apparatus which are in contact with it must be resistant against such corrosion. The pipes that have been used by us for this purpose are lined with rubber. We used a stone-ware pump. The tank in which the aluminum chloride-containing solution is accumulated is built of masonry.

The stones which are necessary for this are applied by the Ceramic Chemistry Firm Berggarten, Siershahn in Westerwald. It is to be noted in the near future so that we shall be able to undertake the necessary conversion at the beginning of the new year.

Apparently the loss which was found in the spare polymerization until now will be reduced through these precautions.

/s/ Dr. Hartmann

(Frame 2264) Notes to German Mineral Oil Co., Stettin, Pölitz, Dec. 23, 1943
from German Vacuum Oil Co. Hamburg-Amühle

Aluminum Chloride Sludge Utilization

When thinking further about the above problem and the questions which are connected with it, we came to thoughts on the basis of which this seems a very important economic question concerning its cost of manufacture, but we are obliged to investigate this question thoroughly in all directions before making a definite decision. Therefore, we intend to present our various thoughts in detail to you.

1) According to the November yield survey there is a total operation loss of 8.68%, and a loss from the polymerization installation of 5.80% which seems unbearable industrially. Therefore, the question of the polymerization loss and thereby the aluminum chloride sludge utilization must be tested very thoroughly from the economic side. Also some of the other losses, for instance the very high filtering loss, which is given at 1.22%, must be reduced.

2) Upon our suggestion you have given your opinion on the matter twice namely, in a letter of Dec. 7 and of Dec. 17, 1943. We cannot see from your letter of Dec. 17 whether the opinion which you express is a retraction of the sludge decomposition itself which you have reported to plan in your letter of Dec. 7.

3) You take the point of view in your letter of Dec. 17 that with regard to the operating disadvantages which the storage causes for you, you want to give the sludge promptly to a third customer without remuneration. We shall not consider in the following considerations whether such a customer can be found. If someone can be found, which we do not consider as impossible, one could probably sell the sludge under the same conditions as bleaching earth, that is, one could probably get 2 reichsmarks per 100 kg. for the mixture product. However, we emphasize explicitly that this is an assumption.

In order to arrive at a value for comparison we must again make assumptions which you will be able to replace by actual numbers in your considerations. We don't know how much sludge is formed at your plant. We estimate a yield of 2 million kg. With the assumed selling price you would get R.M. 40,000. Compared with this one needs to observe the following. According to your letter of Dec. 7, your sludge contains 20% oil from various fractions, a cylinder oil which may be valued at R.M. 180.00, a light lubricating oil at 30.00 R.M., and a gas oil at R.M. 20.00. The average value of the oil is to be taken at R.M. 100.00 from above products. Thus the following calculation would apply. If one can recover 20% oil from 2,000,000 kg. of sludge at an average price of R.M. 100.00/100 kg. then 400,000 kg. of oil would yield R.M. 400,000.00. From this very roughly calculated comparison one can see that one could not justify economically to give away the oil sludge or to sell it at the by-product price.

4) Therefore, we are inclined to have the opinion that the consideration that you express in your letter of Dec. 7 to decompose the sludge itself requires more exact pursuit. In connection with this following questions appear:

a) Can a technical way be found to process the sludge immediately after it is formed so that the oil would not be subjected to any changes? This would make the recovery of the total oil portion possible.

b) What apparatus would be necessary for this, and how much would it cost?

5) If it is to be prepared by yourself, we assume that the aluminum chloride would finally be formed in aqueous solution for which there would be no further use. As we hear this solution is put into the waste water in other plants after diluting it considerably. Is this way possible for you? We do not know whether you have special directions about the make-up of your factory waste water, and if so, whether such instructions can be fulfilled with a strong dilution of a aqueous solution.

Therefore, we should like to ask you to investigate the above briefly-sketched thoughts in detail. We do not claim that they are complete or accurate. We do not have the basis to investigate this further. We are sure that one can find a possibility to solve this urgent problem satisfactorily.

Would you consider it desirable to get rid of the sludge quantities that are stored up at present regardless of the solution of the entire problem? One can naturally get rid of these old storage amounts only without pay. If you are inclined to this, we would ask you for a statement how much storage material is to be picked up, and how the transfer should be done, and what approximate statement could be given to a possible customer about the composition of the storage product.

/s/ Pfefferkorn
German Vacuum Oil Co.

(Frame 2266) To the German Vacuum Oil Co. Office, Dr. Pfefferkorn
Aumühle, near Hamburg, Dec. 17, 1943

Aluminum Chloride Sludge Utilization

Upon your request we let you know that we quoted the following sludge amounts to I.G., 1942, 488,152 kgs., 1943, 630,700 kgs. which is a total of 1,118,850 kgs.

We did not have any freight expenses for this since the deliveries were done collect and the freight was paid by I.G. But we have borne the shunting fee up to 10 R.M. for each car. But it is known to us that sludge runs under the tariff class F.

We have received a supply of 13 tons of recovered oil from this aluminum chloride sludge. But the oil was so bad that we could not utilize it with the best intentions and therefore we did not require further deliveries. Those difficulties we had with the storage and the transport of the sludge are known to you, and we would welcome if you would find a customer for it which would take all the sludge currently. This would, of course, also include the stored quantities which are considerable. We do not request any pay for this because it is a great advantage to save the considerable transporting and storage cost within the plant. We would be very happy if you would name very soon a customer for the total resulting sludge. Of course, we do not request return of the recovered oil.

/s/ North German Mineral Oil Works, Stettin

(Frame 2267) To the German Vacuum Oil Co., Dr. Pfefferkorn, Dec. 7, 1943

Utilization of Aluminum Chloride Sludge

According to your wish we give you the following analytical data about the sludge which is formed.

The aluminum chloride sludge contains an average of 17-20% of oil and 83-80% aluminum chloride hydrate ($AlCl_3.6H_2O$). One part of sludge is completely soluble in half a part of water at 100° with separation of an oily layer. In cold water approximately one part of water is necessary. The oil is separated well from the very acid and corrosive water layer (pH about 2). The oil layer consists of approximately 56% cylinder oil (60 centistokes, 100°C, flash point, 310-320°, solidifying point, -25°); approximately 7% of a light lubricating oil (25 cstk./50°C, flash point, 230°, solidifying point -10°), and 37% gas oil. Chlorine content in the washed oil layer is about 0.1%. In the distillation the chlorine escapes as hydrochloric acid, and the residue oils and distillates are free of chlorine.

We hope that these statements will serve you and we expect to hear further letters with interest. At the same time we report to you that we plan to do the sludge decomposition ourselves.

/s/ North German Mineral Oil Works, Stettin

(Frame 2268) To the Testing Station for Motor Fuel Industry,
Berlin NW7, Nov. 13, 1943

Dump Residue

In our plant the following residues are formed each month:

1. About 7 to 8 tonnes of coke as residue of our cracking plant. The coke consists of 90% carbon, 9% paraffin, 1% ash (water = 0%). It was sold until now to the Thüringesche Kohlen and Brikettverkauf Co., Leipzig. We assume that it was used to carbide steel.

2. About 135 tonnes of aluminum chloride sludge as residue of our polymerization. The aluminum chloride sludge is solid, hygroscopic, and consists of 70% aluminum oxide, 30% gas and cylinder oil. The aluminum chloride sludge was sold until now to the I.G. Farbenindustrie, Ludwigshafen which prepared aluminum oxide from it.

3. About 23 tonnes of used bleaching earth as residue of our refining. The bleached earth consists of 50% oil and 50% ash. It was sold until now to Spangenberg Works, Hamburg-Eidelstedt, which centrifuged the oil out of the bleaching earth.

4. About 15 tonnes of thin mashy sludge with a oil content of about 35%,2-3% ash, the rest water, the oil sludge has been sold to the United Asphalt and Tar Products factory, Hamburg-Altona. They probably used the oil sludge for the manufacture of camouflage dyes.

5. About 8-10 tonnes of waste hydroxide. In recent time there is formed a 10% solution of sodium salts of organic acids in the deacidizing of our olefins. The hydroxide was not sold until now.

We hope that the above statements will have served you and we are always willing to give further information.

/s/ North German Mineral Oil Works - Stettin

(Frame 2269) To I.G. Farbenindustrie, Inorganic Division: Att.: Dr. Hühn,
Ludwigshafen, Aug. 10, 1943

Deliveries of Aluminum Chloride-Containing Sludge

~~We acknowledge gratefully receipt of your letter of Aug. 4, 1943.~~

We are sorry we cannot send you the desired concentrated aluminum chloride solution, since we have charged it only in a large experiment in order to test a suitability of a nozzle which was made available to us by Leuna for sludge decomposition. We undertook the decomposition in an apparatus neither rubber-lined nor made of masonry, since no other was available to us.

As we expected there occurred strong attacks of the concentrated aluminum chloride solution on pipes and pumps. As soon as we have converted 10 tonnes of sludge and determined that the decomposition ran without objection, we have taken out the aluminum chloride solution in order to save our apparatus. Only a small sample was tested in the laboratory, whereby we determined that the content of aluminum chloride amounted to 6%. The sample was oil-free and relatively light. The separation of the oily portion was done without difficulties. According to our opinion there is no reason to assume that the decomposition would not occur just as easily in larger amounts, as in our 10 tonne experiments. The solution can doubtless be brought to a very high concentration. So far as we remember, it amounts to 30 % aluminum chloride.

With interest we acknowledge that you may be able to make suitable tank cars available to us for transport of the liquor. Also we shall try to obtain such cars and will let you know accordingly.

At present we are having a certain apparatus built and made corrosion-safe, this will take a few months. As soon as we know the time at which we will be able to deliver aluminum chloride solution we will let you know.

/s/ North German Mineral Oil Works, Stettin

(Frame 2270) To I.G. Farbenindustrie, Inorganic Division, Dr. Hühn, Ludwigshafen, July 29, 1943

Delivery of Aluminum Chloride-Containing Sludge

We have let you know sometime ago that we shall try to utilize the resulting aluminum chloride-containing sludge in the same manner as it is done in Leuna in the plant of Dr. Zorn. We have good results in our experiments, and we plan to convert such a manufacturing station as soon as possible. This means that we cannot deliver solid aluminum chloride-containing residues from now on, but aluminum chloride in solution. So far as we remember, you would be satisfied with this form of delivery.

We ask you to let us know whether aluminum chloride-containing solution which you obtained from Leuna is delivered in acid containers or in rubber-lined tank cars. Also, we want to know whether Ludwigshafen could give us suitable vessels or cars. The full daily load of our works would yield about 15 cu. meters of a 30% aluminum chloride solution. We hope to hear from you soon.

/s/ Dr. Hartmann, North German Mineral Oil Works, Stettin

(Frame 2271) To I.G. Farbenindustrie, Ludwigshafen to North German
Mineral Oil Works - Stettin, 11/27/42

Concerning Aluminum Chloride-Containing Sludge

We acknowledge gratefully the receipt of your letter of the 21st of this month.

We are very much interested in the fact that you are still trying to free the aluminum chloride-containing sludge of the oil which is adherent to it. We hope that your laboratory experiments will soon lead to practical results.

We did not separate the oil from the sludge by extraction, since we did not have the necessary extraction apparatus and processing plant. It is true that once at a discussion at Oppau one talked about cleaning the sludge by extraction with benzol. These experiments were suggested by Dr. Baumeister and could be confirmed by us. One obtained an almost purely white aluminum chloride-containing powder which can be transported easily in wooden barrels or lime cars. The benzol necessary for extraction can be recovered through distillation and thus be used in a cycle.

We processed the sludge in the following manner. We put it into water so there results in approximately 25% aluminum chloride solution. In order to make the separation of the liquid from the oil-containing portion easier, we heat the mixture after addition of Dismulgan VIII to about 80-90°. After about 12 hours standing one obtains in this way a clear aluminum chloride solution which can be separated from the oil that settled on the surface.

In the future about 40-50 tonnes per month of this waste oil will be formed for which we do not have a customer so far. The question of utilization of this oil is among others to be discussed immediately. According to investigations undertaken by us we are concerned with superheated steam cylinder oil of a specific gravity of 0.900 and a flash point of 295°C and a viscosity of 9-10 Engler at 100°. The other data obtained so far are solidifying point -12°C, coke test 6%, ash 0.05% and asphalt 0.0%. We ask you for your suggestion whether this oil could be processed in your plant or whether you could name someone who would be interested.

If the purification of the sludge should be possible by yourself in Pölitz, then this question would answer itself. We would be very happy about this for the following reasons: The storage of the sludge is only possible under great difficulty, and in the future we will have to get specially lined acid-fast tanks. Also the unloading of the sludge car can hardly be done in the unloading time allowed by the state railroad.

We look forward to your answer in this matter with interest.

/s/ I.G. Farbenindustrie

Frame 2273 Stettin-Polits, Feb. 25, 1942 - Memorandum

Concerning Aluminum Chloride-Containing Clay From Sludge

Laboratory tests have resulted in the following data. Upon processing of 500 grams of olefins and 5% aluminum chloride (equals 25 grams) about 90 grams of sludge are formed. Upon mixing of 500 grams of this sludge with 75 cc of water (equals 15.2%) in the presence of 500 grams of gas oil there result 808 grams of oil and 203 grams of clay. The temperature rose from 20 to 64°C without being cooled from the outside.

About 200 grams of a superheated steam cylinder oil are formed in the processing of the oil.

Viscosity 9.3 Engler° at 100°C
Viscosity index 98
Flash point 315°
Aniline point 134°
Solidifying point -18°C
No asphalt is contained in the oil.

In addition to that 39 grams of an oil are recovered which boils between 230-270° at 1 mm mercury.

Viscosity 9.99 Engler° at 38°C
Viscosity 5.54 Engler° at 50°C
Viscosity 2.19 Engler° at 80°C
Viscosity 1.67 Engler° at 99°C
Viscosity index 82
Solidifying point -36°
Flash point 202°

In the processing of 500 grams of olefins there also result 36 grams of clay which contains aluminum chloride, 36 grams of superheated steam cylinder oil and 7 grams of thin oil.

/s/ Hartmann

Frame 2274 From I.G. Farbenindustrie, Ludwigshafen, to North German Mineral Oil Works, Stettin, Nov. 1, 1941

Concerning: Aluminum Chloride-Containing Sludge from the Mineral Oil Synthesis

Sometime ago we obtained from you several cans of aluminum chloride-containing oil sludge which was formed in the mineral oil synthesis. It has been shown in the processing that this sludge contains considerable amounts of tar-like constituents. In separating the aluminum chloride solution which is formed upon decomposition with water and the low viscosity oils by centrifuging they smudge badly. There centrifuges are completely stopped up after a short time and are very hard to clean.

Upon suggestion of Dr. Hartmann it was tried to extract this sludge with hot benzol before treating with water. By the extraction with hot benzol almost all oil-containing constituents could be removed. A light almost entirely oil-free product remained which was very easily decomposed by water.

We consider this extraction of the oil sludge with hot benzol absolutely necessary. Perhaps one could recover a usable oil by this method from the benzol extraction after distillation.

Therefore, we ask you to test whether this benzol extraction could not be carried out at Polits because as we have said before, it is absolutely necessary to recover the oil. Thereby you could probably cut down the cost of transportation through eliminating the extra weight of the oil to about half the price.

/s/ I.G. Farbenindustrie

Frame 2276 I.G. Farbenindustrie, Ludwigshafen, Dec. 3, 1940 - To the North German Mineral Oil Works, Stettin, Att.: Dr. Hartmann

Concerning: Residue from the Polymerization and Paraffin Pre-Purification

We return to your last visit at our Ludwigshafen plant and to our discussion of the above matter, and remark that in a further investigation of this question concerning the transfer, a few unclarified points were pointed out. We would like to ask you to let us know your decision about this matter as soon as possible with regard to the following points.
During the manufacturing process in Building SP 744 of the lubricating plant, there accrue bleaching earth and $AlCl_3$ sludge. In detail: 1) Bleaching earth from the paraffin purification, 2) Bleaching earth from the bleaching earth plant, 3) $AlCl_3$ sludge from the polymerization, 4) $AlCl_3$ sludge from the paraffin purification.

To 1) and 2) The bleaching earth falls from the filter presses directly into the trough tipping device, then it is brought to an intermediate storage which has a roof and is then to be transported into another plant for washing. It is still to be clarified in what form and in what kind of car this transport is to be carried out. Also, the intermediate storage for it is yet to be determined.

To 4) it is assumed that the $AlCl_3$ sludge falls from the separators through a pipe line into a vessel of about 2 tonnes content. Then it is to be gotten to a normal railway car in our Ludwigshafen plant for further processing. This kind of transport causes difficulties because the processing station of the Ludwigshafen plant does not have arrangements (crane) for unloading and emptying. Also it is not planned now to procure the appropriate arrangements. All residues which are processed at Ludwigshafen at present are liquids and no loading difficulties occur in those products.

The round containers that were suggested during the last conference are not well suited for transport inside the plant and they are difficult to empty.

In case that the Ludwigshafen plant cannot procure unloading arrangements we make the following suggestions:

The transport of $AlCl_3$ sludge from the point of formation to the junction track of the lubricating oil factory occurs in troughs which can be tilted and where the troughs are removable. They are loaded on the prepared railway cars by a crane thereby the car frames remain at the Pölitz plant for further use. The unloading in Ludwigshafen is done with the aid of the existing crane arrangements at any point on the four available car frames. These are then to be brought to the processing point by means of tractors and if possible tipped directly into the available stirring container. The empty troughs go back to Pölitz.

A further difficulty occurs in the fact that this sludge solidifies into a solid substance because of its paraffin content. Probably it will not be loosened from the container walls by tilting, and also a breaking up of the whole sludge cubes is difficult to carry out. Perhaps it is possible through putting paper around the troughs before filling, and by further use of as much paper intermediate layers as necessary to divide the large clay block and to make the emptying easier that way.

To 3) The $AlCl_3$ sludge from the polymerization is thickly liquid and it causes difficulty in removing it from the containers. The transport could be done in the same tilting troughs as in number 4).

According to description of the operation there result daily 4 tonnes of aluminum chloride sludge, together thus there are 8 tonnes. If one takes the tilting trough with each 2 tonnes content, and a load per car of 15-18 tonnes, then each other day a car with 8 troughs leaves the Pölitz plant. According to information of our dispatcher, a car from Pölitz to Ludwigshafen and return including shifting and unloading time would take 24 days. In order to carry out frictionless (without difficulty) transport, it would be necessary that about 100 troughs and about 20 car frames would be necessary. The price for one trough with cover is about 250 R.M. and for the underparts about R.M. 350, thus the suggested transporting means would cost a total amount of 32,000 R.M. Considering a possible storage of filled troughs in the Pölitz and Ludwigshafen plants, the number of apparatus that is to be ordered must be tested again. Further, the Pölitz plant would need another loading place and also another intermediate storage.

With regard of the named difficulties, the question arises whether, with regard to economy, another method for processing of the sludge residues should not be looked for.

We ask you to test the questions named, and hope that at your next visit you will have a final clarification.

Translated Oct. 28, 1946 - Rochelle H. Bondy

Checked Nov. 27, 1946, - CCM

S.O. Devel. Co. of N.J.

TECHNICAL OIL MISSION

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Reel 79, Item 134, Pages 2694-2695
June, 1943

III. Constitution of Lubricating Oil
(Dr. G. W. Nederbragt)

Subject under Investigation: Determination of Viscosity up to About 350°C.

Introduction:

In the preceding report, the viscosities of the branched chain paraffin hydrocarbons 10-nonyl nonadecane and 7,12-dimethyl, 9,10 di-n-hexyl octadecane were given. With both materials, the viscosity was higher at lower temperatures and lower at higher temperatures than in the case of the corresponding normal paraffin isomers. In order to ascertain whether this is also the case with other branched chain hydrocarbons, the viscosity of 2,2-dimethyl-n-docosane has been measured.

Summary of the Investigation:

The densities tabulated below were determined with the aid of a pycnometer of approximately 1 ml. capacity with a long calibrated stem; the viscosities were measured with a falling ball viscosimeter.

Density and Viscosity (Falling Ball)
of 2,2-Dimethyl-n-docosane
$C_{24}H_{50}$

Temperature	Density	Viscosity Dynamic (Centipoises)	Viscosity Kinematic (Centistokes)
39.9	0.7830	8.50	10.86
80.2	0.7565	3.26	4.31
133.2	0.7216	1.471	2.04
183.7	0.6887	0.840	1.219
245.4	0.6473	0.499	0.771
283.2	0.6193	0.380	0.614

These viscosities bracket those given for 70-90°C. in Report No. 8975 of Dr. von Mazee in which a value of 3.26 centipoises at 80°C. is recorded. The latter viscosities were measured with an efflux capillary. (See Abb. 5773-2-133)

Conclusion

In contrast to the 10-nonyl nonadecane and 7,12-dimethyl, 9,10-di-n-hexyl octadecane, which are less viscous at higher temperatures than the corresponding n-paraffin isomers, we have found that 2,2-dimethyl n-docosane remains more viscous at 284°C. than n-tetracosane.

Future Program

The viscosities of several materials with long carbon chains, and which also contain an atom of oxygen, will be determined and compared with hydrocarbons of similar structure.

(Translator's Note: Immediately preceding the above article, a graph is given (microfilm page #2693) which shows dynamic viscosity in 10^{-3} poise on a log scale as a function of temperature over the range 0°C.-300°C. Curves for 7, 12-dimethyl 9,10-di-n-hexyloctadecane, 10-nonylnonadecane, 2,2-dimethyl-n-docosane, n-$C_{16}H_{34}$, n-$C_{24}H_{50}$, n-$C_{35}H_{72}$, and n-$C_{43}H_{88}$ are given. This graph is apparently an attachment of a preceding report.)

GECW/igm

Translated by G. E. C. Wear
Esso Laboratories-Research Division

Standard Oil Company (Indiana)

INFORMATION DIVISION TRANSLATION T46-74

API-TOM Reel 79, Frames 2349-2366

Short Survey about the Work of the Division for the Combatting of Plant Diseases of the Laboratory of the N.V. de Bataafsche Petroleum Mij. in Amsterdam

Introduction

It has been known for several decades that a few mineral oil products can be used for combatting pests. In the years between 1920 and 1925 the use of mineral oil emulsions for the combatting of diseases of citrus orchards in America increased much. Preparations from pyrethrum extract solution in odorless kerosene were accepted as insecticides in the household. The laboratory added the study of these combatting agents (1).

The study of this subject led soon to the production of the product Shelltox which corresponded to the requirement of cheapness, and whose manufacture was stopped in Europe only since no more kerosene is available for this product.

II. Earlier Investigations

(a) Oil Emulsions

With the help of the already-known data, and by means of a number of single experiments that were carried out in the laboratory, an oil emulsion TPR60 was compounded, starting with white oil. It was examined practically in 1937 and 1938 in Palestine and was investigated in direct collaboration with Mr. Blijdorp of the laboratory. The final product that was made in Palestine and Algiers was only barely satisfactory, and is certainly in need of an improvement still. Because of the international tension in 1939 and the war these investigations had to be stopped for a time.

It has been found that outside of the citrus area in Europe there existed a market for mineral emulsions namely, the combatting of the red spider (Paratetranychus pilosus C & F) as well in winter (WE 103 as in the summer (ZE 60)).

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(1) Those who wish to know more about the history are referred to the publication by J.Ph. Pfeiffer and P.A. Blijdorp entitled "The Use of Mineral Oil Products for the Control of Plant Diseases." This was published for the occasion of the Fifth International Technical & Chemical Congress of the Agricultural Industries held in Scheveningen in 1937.

The preparation and sale of the latter emulsion (TPR 60), which is known in the Netherlands by the name ZE 60, was not pushed because of patent claims of a third party. These do not exist any more but now the necessary white oil is lacking.

After the two oil emulsions have been prepared in the laboratory and after working out of their commercial production they were subjected to extensive laboratory investigations and experiments in practice. Thereby it was tried to determine physical requirements which such emulsions must fulfill by studying the oil deposits on the plant after spraying. One differentiated between "initial oil deposit" and "total oil deposit".

These agents are also important under the present conditions, because the orchard carbolineum, which has been used for winter treatment of fruit trees for a long time, kills the leaf louse eggs, but not the eggs of the red spider. Because the winter emulsion WE 103 did not result in sufficient combatting of leaf louse eggs, a new winter emulsion has been developed by the admixture of 2% dinitro-o-cresol to WE 103, calculated on oil. This unversal winter spray WU 117 showed satisfactory results in the laboratory and in practice for the combatting of the red spider and the leaf louse (2).

The constant increase of demand of this product, the business of which was increased in the Netherlands from about 40 tonnes in 1938-1939 to 490 tonnes of the product in 1943 demonstrates the suitability of the product. The summer emulsion was not so effective, while disregarding the fact that the white oil necessary therefor was no longer available, the growers avoided using this means when also California liquor had to be sprayed against scab. It has been shown that in this case burning is experienced on several varieties.

(B) Gas Insecticide

Investigations were carried out in the field of gas insecticides, particularly with M-gas, with methyl allyl chloride which is prepared by Shell Oil Co. of California. This gas proved itself very usable for the killing of insects in grain and tobacco and materials of plant and animal origin (3).

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(2) See also publications by P.A. Blijdorp entitled "Universal Ovicidal Action of Special Mineral Oil Washes with a Winter Wash for Deciduous Fruit Trees", read at the Seventh International Congress for Entomology in Berlin, August 1938.

(3) See the doctor thesis of Dr. C.J. Briejer, Methyl Allyl Chloride as a Fumigant against Insects Infesting Stored Products.

Because of the war no new supplements of the limited supply in the Netherlands could be effected. Therefore the sale was not pushed much. But the gas is used regularly for various purposes with much success. The quality of the residual stock has declined considerably. When this product can again be produced at a cheap price one can expect an appropriate market for it.

III. Current Investigations

A. Method

During the investigations of the period before the war it was established that small variations in the formulas may have a relatively great influence on the biological action of the preparation. In dinitro-o-cresol preparations the pH of the spraying liquid has much influence on the killing of leaf louse eggs. It has also been found that cresol which is incorporated in WE 103 as disinfectant, on the casein basis has a stimulating action. This harmed the ovicidal action of the WE 103 while the DNK, that was used in WU 117 in a dosage of 2% on oil for the combatting of the leaf louse, influenced the toxicity for red spider favorably. Upon closer investigation it was found that phenol, which is used for the same purpose as cresol, increases the limiting surface tension of oil to water phase in oil emulsions containing agral (agar?) and thus it decreases the surface action.

Since agar, which until this moment was a normal constituent of WU 117, cannot any longer be obtained because of the war, it was found that the action of this spraying agent was markedly improved through elimination of this constituent. Similar experiences were also had with other combatting agents like insecticides and fungicides.

If one wants to work out a formula as favorable as possible starting out with a given starting material, one has to investigate a large number of variations and combinations. This is entirely impossible in practice, because these experiments take too much time, work and money. The solution for this problem exists in the working out of laboratory methods which make it possible to investigate a large number of preparations in a short time. This method would have to give reliable indication about the effectiveness in practice. After these laboratory investigations a few of the best combinations are tested thoroughly in practice.

These considerations lead us to use a considerable part of the available time since 1939 in developing this kind of method, and in the comparison of the results so obtained with those of practical experiments in the field and orchard.

a) Method for testing of wetting agents

In previous examinations for the determination of wetting action glass plates that were covered with carnauba wax were used and the wetting was examined visually after submersion in the liquid in which it was to be investigated. This method is only suited as a comparative measurement in a few cases but does not yield numbers which are a direct measure for the wetting action in practice. Therefore, an investigation for other methods was undertaken whereby boundary angle measures were carried out, which determined the surface tension and limiting surface tension according to various methods, and the preferential wetting of oil and water was tested on various surfaces.

After a time these investigations were broken off because of lack of time and because no results appeared that made successful application in practice probable. In the meanwhile, we found important indications about the influence of the method of using the spray liquid and the kind and amount of the wetting agents that is to be used on the killing action. These indications give the impression to agree well between the test and practice.

b) Methods for testing the Fungicide Action

A method for the determination of fungicide action was worked out which was planned (4) as an investigation for an exchange agent for copper and sulfur as fungicides. On basis of that investigation we are still working regularly at perfecting this method and its transfer to practice.

The following fungi are generally used for these investigations:

1. Venturia inaequalis (scab in apple)
2. Venturia pirina (scab in pears)
3. Cladosporium fulvum (false mildew on tomatoes)
4. Phytophthora infestans (potato disease)
5. Ascochita pisi (root disease in peas)

c) Methods to Test Ovicidal Action

Another method which was worked out in a certain degree completely is the determination of the ovicidal action of spraying agents with the aid of meal moth eggs (Ephestia kuhniella Z) (5).

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(4) See for this K. Hartsuiker "Het wetenschappelijk onderzoek van Fungiciden". Academische Doktorschrift, Amsterdam, Sept. 1940.

(5) See for this the Doktorschrift of Dr. G.E.E.H. Dierick, "De ovicide werking van winterspree-immiddelen bestudeerd in het Laboratorium", Amsterdam, Nov. 1942.

Thereby indications were obtained by the action of winter spray agents on a biological object which is not bound to seasons, and whose life cycle made it possible to collect data throughout the whole year each fourteen days.

Because it is of primary importance for these laboratory methods to be able to obtain reproducible values as possible throughout the whole year the investigation was prosecuted in two directions after the preliminary finishing off and publication of the method. They were (1) further normalising experimental conditions, (2) influence of the manner of utilisation of the spray liquid.

These investigations which are still in progress led already to important improvements and new insights.

Experiments that are conducted with insects other than those that must be combatted in practice never lead to definitive conclusions. Also the difference between this type of laboratory investigations and the spraying in practice is too great. Therefore methods have been worked out to do laboratory experiments with insects that have to be actually combatted, for instance, red spider, leaf louse and frost spanner. Thereby, satisfactory results were obtained, particularly with red spider. This was known as an insect with which one could not experiment in the laboratory, and which can now be evaluated very well with the method now used.

These experiments were worked out while in 1943 with 400,000 meal moth eggs and in the winter season 1943-44 with about 60,000 eggs of the red spider and about 30,000 eggs of leaf louse, and 30,000 eggs of the frost spanner.

d) Methods for testing insecticide action

Methods for testing summer spray were worked out with leaf louse similarly as for winter spray means. It was first very difficult, because the experimental subject moved about very much.

Thus an apparatus was constructed through which it was possible to dose the spray that was to be examined exactly on the experimental subject.

Secondly, an insect was sought which would be available throughout the whole year, or at least during a large part of the year. We have not yet succeeded in finding a subject which, like the meal moths, can be cultured in simple manner throughout the whole year, and for purposes of combatting has characteristics sufficiently similar to those of the leaf louse, which is to be fought.

We decided, therefore, to breed and use a number of different kinds of leaf louse, which were so chosen that they are available during the greatest part of the year, and namely: Peach louse (Myzus perdicae, sulzer) on different hot house plants in February, March and April; Black bean louse (Aphis fabae F.) on great nasturtium in May and June; Reed (Trans.: cane or bamboo?) louse, (Hyalopterus/arundinus F.) in July, August and September and in the first half of October; and willow louse (Lachnus salignus Gmelia) in the second half of October, November and beginning December. The growing of lice in the hothouse still leads to difficulties, among others in connection with the limited room which is available.

A special technique was developed in which these moving animals could be established on a substrate suitable to them, without injuring their life-force. This technique made possible the control of the number of destroyed and surviving animals.

The eggs of the girdle-spinner (Melacosoma neustria L.) were used successfully for the study of the action of combat materials on caterpillars (larvae). These eggs can be retained for about a year in the refrigerator and incubated at room temperature at the desired moment.

Supposing that the demand is known at least a month in advance it is possible in this way to have available at each moment living and sufficiently viable caterpillars. The difficulty here lies in the collection of a sufficient amount of eggs in Autumn and in the removal of a frequently occurring disease (the polyhedron-disease). The use and the dosage of the combat means seems like that against the leaf lice.

Also silk worms were used in these investigations.

e) Methods for Testing the Phytocidic Action

In addition to the lethal action of disease-combatting agents on the disease-causers, it is also of greatest importance to study the phytocidal action on the culture plant that is to be treated. In order to avoid considerable plant damage by the use in various experiments of preparations in different concentrations, it is necessary to develop a laboratory method which will permit coming to an impression about the phytocidal action of the agent.

Cucumber plants from the greenhouse were used for this purpose. These can be available almost all year. In the winter we also used wild apple seedlings which have been brought to sprout in the greenhouse. The value of indications that were obtained in this manner were controlled during the suitable season in nature by spraying plants that are to be treated.

A method was worked out whereby the damage can be determined by photographic contact pressure. Because of lack of photographic material this method was not used to a great extent.

Concerning the phytocidal action of mineral oils, it was found that the occurring damages are caused mainly by the attack on chlorophyll of the leaves. A method was worked out which makes it possible quickly to obtain an impression by means of chlorophyll extract about the phytocidicity of more-or-less refined oils that have been prepared especially for this purpose. Results so far show good correlation with damage during spraying of cucumber plants.

Also, the development of a purely scientific physiological method for the study of phytocidal action of combatting agents was started. The influence is observed of these agents on transpiration and root breathing of bean plants that have been grown under very exactly-controlled conditions. On account of lack of time and the large amount of work to which the investigation toward a usable method must lead, these tests proceeded only slowly.

B. Development of New Products

(a) Shell Nitrum

After the beginning of the war nicotine became scarce. But the laboratory still had a quantity of pyrethrum extract which could not be used in the production of Shelltox. An exchange agent (substitute) was concocted on the pyrethrum and ester salt basis. Through special processing a clear, homogeneous solution was formed.

This product was first thought to be only a substitute agent. But it was proven of such good value in practice that one had to consider whether it will not remain a permanent commercial product when ester salt and pyrethrum extract will again be available in sufficient amounts and at reasonable prices.

(b) Shell Nitroleum

In 1941 the amount of tar oil fraction which had been used for the preparation of fruit tree carbolineum was so restricted that one had to look for a substitute for the season 1941-1942. Since there was no time to conduct experiments in practice or even in the laboratory on the subjects that had to be combatted, therefore, starting with the experiments that had been conducted with meal moth egg, a preparation of dinitro-ortho-cresol basis (DNK) was made which deviated considerably in kind and composition from known products that had been used in this field. We expected that it would be effective in considerably lower concentrations.

But it has been found in practice that this preparation, whose activity is based on the action of the acid dinitro-ortho-cresol (HDNK) dissolves in insufficient amount in the cold dilution water whose temperature in practice is only slightly above 0°C. Thus the action was unsatisfactory. The composition therefore had to be changed for the season 1942-1943. This complaint was eliminated, although the DNK concentration in the spray liquid has to be increased. Satisfactory results were obtained with this product in 1943 and 1944.

Very many chemical biological investigations had to be carried out for the development and production of this agent. One of the investigations includes the working out of a quick reliable analysis method for the determination of the DNK content during the nitroleum production. This method has been proven very good in practice.

(c) Combatting Agent for Fungi

The Division of Gardening of the Department of Agriculture carried out experiments to find some substitute for copper which is difficult to obtain for the combatting of fungi. The phenolthiazone which is known from the American literature has been considered particularly important.

It was sought to produce this product commercially by understanding with the government. From this we planned to prepare an agent for combatting of potato disease (phytophthora infestans) and of the apple scab (venturia inaequalis and venturia pirina). The preparation of phenolthiazone as well as the composition of this agent leads to too great difficulties, because of the present shortage of raw materials.

C. General Investigation of Insecticides for Summer Treatment

A general investigation for materials that are suited to combat insects was undertaken. This investigation has to be preceded by a study of the connection between chemical structure and toxicity. For this purpose a series of various material, among others benzene, naphthalene, and tetrahydronaphthalene derivatives, were prepared in concentration of 0.5% and their insecticidal action was investigated particularly for leaf louse.

First we looked for a generally usable method to convert these materials into sprayable form with auxiliary agents which themselves were not toxic or very little toxic. Nicotine was used as comparison. Although these experiments are still in progress, the following has already been found:

Certain groups like -CNS, -CN, -C-CCl_3, and to some extent -Cl generally increase the insecticidal action. That does not mean that organic materials which contain these groups have a distinct insecticide action. It seems necessary that the structure of the organic material which contains such a group satisfies other requirements before they show the distinctly insecticidal action. It could not be found from this investigation which these requirements are. Factors that have been closely examined in this connection like size of the molecule, steric configuration, adsorptability, dipole moment, etc. did not result in guide lines. (most suitable methods). This may be because these factors are known insufficiently in many cases. Also a number of trichloroethane derivatives and some tetrazonium compounds and aliphatic rhodane derivatives were examined.

D. Experiments in Field and Practice

(a) Winter Agents

Since only indications and guide lines can be obtained with experiments in the laboratory, the usability of combatting agents have to be tested finally in practice. Therefore, extensive experiments were conducted in each season. They can be divided into three groups each, according to the stage of development of the spray.

1. Spraying in the experimental garden of the laboratory.
2. Spraying by friendly growers in their own administration.
3. Spraying cooperation with "Plant Breeding Service" in Wageningen.

The first practice spraying with new combatting agents were always carried out under #1. Here too large concentrations could be sprayed without complaint. Thus the margin with regard to damage to plant could be studied.

Agents whose action and phytocidicity limit has been determined, but whose composition for commerce has not been determined definitely, were examined under #2. The results that were obtained remained here therefore exclusively for the knowledge of the laboratory.

Agents whose final composition was relatively firmly established were sometimes tested in various concentrations like group 3.

The influence of conditions in various regions of the land and in consecutive years may be very different. Also the action of the agent on various types plant and varieties may be very different. Therefore, these experiments had to be very extensive and had to be repeated for several years.

The control of the results for the parcels which had been treated apparently successfully was done in the following manner. At several intervals the number of insects on 50 or 100 leaves or buds per tree were counted. Also they were evaluated visually at a later time, and finally by control of the amount and quality of the harvested fruit. In 1943 experiments were carried out in the field with WU 117 prepared from various batches of spindle oil in order to be able to test, among other things, the influence of the flow point. It is tested with WU emulsions with low pH and with nitroleum (the DNK containing preparation) as substitute for fruit tree carbolineum. The combatting of apple leaf lice, red spider, and apple blossom stinger were tested. In 1944 also the frost spanner was watched closely. Further we studied the suitability of cooking cycle stock for the use as oil base for winter combatting of the leaf louse and red spider.

(b) Summer Agent

The action of Shell Nitrum and ZE 60 oil was controlled in similar manner.

(c) Killing of Potato Tops and Leaf Eradication by Spraying

Preparations with DNK as their most active constituents have been proven usable for the killing of potato tops and leaves. Research with Shell Nitroleum that was carried out in cooperation with the "Plant Breeding Service", proved that this product is very well suited for this purpose. It was possible to determine the concentrations that are to be used.

(d) Use of M-Gas

The small supply of methallyl chloride that was still available in Holland at the outbreak of war could not be sold free from objection because of its properties. It is now gradually used in the fumigation that was introduced by B.I.M. The personnel of the laboratory makes the plans and supplies technical aid.

IV. Planned Investigation

A. Investigation Methods in the Laboratory

As mentioned before in the investigations that have been carried out so far the necessity has become apparent to have laboratory methods available which would make it possible to obtain, in a short time and independently of the season, reliable data about the suitability of chemical materials or compounded agents for the combatting of one or another plant disease. The results that are obtained with this method must above all be reproducible so that new data can be compared with old data.

This necessity becomes particularly apparent if one finds that without such methods it would be almost impossible to obtain opportune material to oppose Netherland patent claims in time for which the deadline is only four months.

Most of the investigation methods that are found in the literature are only insufficiently described. The study of the publications always lead to the conviction that they do not suffice in any way for the above named requirements.

Investigations for the development of such a method are in progress. But the study of the following points has to be started yet.

1. We must test how far the reproducibility can be increased.
2. One has to determine the correlation between results obtained by these laboratory methods and (1)with those that were obtained in the laboratory with the active material to be used for combatting, (2) with those that were obtained in practice.
3. Investigations whose changing would lead to improvement of this correlation.

This amounts (in the case of laboratory methods) to the study of physical properties of combatting agents such as wetting, clinging, rain-resistance, stability in transport and storage stability.

So far as fungicides are concerned particular importance has to be given to the evaluation of rain stability. Investigations in recent times have proven that it is possible by the methods used to compare the rain resistance of various fungicides with each other, but this method has not been developed enough that it would be possible to predict whether or not a fungicide would be sufficiently rain-resistant in Netherlands practice. So far as the investigation method for insecticides is concerned one can state that this method is sufficient for the determination of their activity on leaf lice. This method can also be used with success against other insects, for instance against larvae. The collecting of a sufficient number of larvae of approximately equal resistance for this experiment is difficult. It will be tested in which manner it is possible to obtain reliable results with the smallest possible number of larvae.

As far as investigation methods for ovicidal oil-containing agents is concerned, we shall test which manner of dosage of oil emulsions gives results which can be best compared with practical spraying. For this purpose, six dosage methods of oil emulsions were compared, prepared according to different recipes.

The investigation regarding phytocidicity in the physiological way (study of transpiration and root breathing) was pursued.

B. The Investigations for New Plant Disease Combatting Agents and Improvement of Existing Agents.

(a) Development of Insecticides

Various newly prepared organic compounds are examined for their effectiveness on leaf lice, larvae and a few other insects. Many compounds that have been tested for their activity on leaf lice last season were investigated this year for their effectiveness for larvae and other insects.

Further it will be attempted to combine insecticides in order to combine as many of the favorable properties of various insecticides as possible. A few materials will be tested as fumigants.

Finally, it is our intention to make further investigations for the combatting of the cochineal insect in citrus culture. For a long time oil emulsions have been a promising agent for these. These experiments will have to be carried out mainly and preferably under conditions similar to the practice. Because the combatting of Cochineal insect is so difficult in laboratory investigations, these investigations shall not be started until more data about the effect of typical properties of oil and oil emulsions on the killing action are available. Therefore, the intent to wait for the results of the experiments that are named under sub "b" with regard to ovicidal action.

(b) The Development of Ovicides

Various organic compounds named above were used in spring for their action on eggs of the red spider. The hatching of the eggs is controlled as a rule. It will depend on final results whether still other organic compounds will be tested as ovicides this year (from meal moth eggs).

An extensive investigation is planned about the influence of typical properties of oil emulsions on the effectiveness of the same as an ovicide. Particular attention is to be paid to influence of stability and the particle size of these emulsions and the action and the influence of various emulsifiers. It will also be tested how far oil deposits on the object treated depends on these factors. These investigations will be continued this year. The final purpose of these fundamental investigations is to obtain a better knowledge of the factors which determine the activity of oil emulsions. In this manner we hope to obtain directional indications for a most practical composition of our oil-containing combatting agents.

These investigations are closely tied with the investigations named above for the method of dosing oil-containing agents.

(c) Combined Combatting Agents on the Oil Basis

In our Shell WU 117 we have an oil emulsion for winter treatment of fruit trees, as well as a good combatting agent by means of the oil, also satisfactory for leaf louse fighting.

Our summer emulsion Shell WE 60 is only suited for combatting the red spider. It will be tested whether with the aid of materials named under sub (a) or other insecticides there can be compounded an emulsion which will be also insecticidal. Such combinations are so advantageous because they can reduce the large number of sprayings which a serious grower must carry out in the course of summer, which can lead as well to a saving of working force as well as naphtha.

(d) Development of Fungicides

It is of utmost importance to find a fungicide that can be combined with ZE 60. Scab combatting in the summer is done almost exclusively with California liquor. It seems that this agent, combined with oil emulsions, causes leaf burning many times with sulfur-sensitive varieties. A fungicide that could always be combined with oil would be very advantageous in connection with the market for our summer emulsions. A search for a oil emulsion which can always be combined with California liquor would be important as an alternative. We have started investigations in both directions. Among other things phenothiazone which has been mentioned (on page 11 and 12 in the original) was tested as the fungicide.

(e) Investigations of the Phytocidicity

All combatting agents that are promising under a to d will be tested for their phytocide action. This will be done on the plant for which the combatting agent is to be used, as well as on cucumber plants, the general object for the phytocidicity investigation. Further, an investigation is in progress regarding the influence of refining and the degree of refining of oils on the phytocidicity of emulsions compounded with these oils. This investigation, which until now has been carried out with spindle oil from asphaltic crude material, will proceed with oils from paraffinic crude. The influence of viscosity of the oil on the phytocidicity will likewise be investigated.

(f) Improvement of the Existing Agents

The paste-like Shell Nitroleum which has been put on the market by us has the disadvantage that it must be sold in glass returnable-packed containers which hinders the selling, and the production costs are high. It will be tried to produce a pulverized product which can be sold in paper containers without losing the advantages of the agent that has been developed by us.

G. Larvae Glue ("Lime")

We think we can expect that we will succeed to produce a well-suitable larvae lime which contains chlorinated paraffin as most important constituent. From the suggestion of Prof. Zerbe it will be investigated what will be required of chlorination products of various kinds of paraffin, and heavily paraffin-containing products in order to make them most suitable. As soon as these data will be known, it will be tested which other starting materials, particularly those of the oil industry, can be mostly considered, and which is the most favorable composition of larvae glue.

H. Emulsifiers and Wetting Agent

Various sulfonic soaps that were produced by the oil industry and Mersolate (and related products), will be tested for their suitability as wetting agents and dispersers for oil and other things in water-soluble materials. This will be done with regard to preparation of plant disease-combatting agents. We have acquired them through Prof. Zerbe.

I. Experimental Spraying

Experimental spraying in the experimental garden of the laboratory or at friendly growers will be carried out with combatting agents whose laboratory tests have progressed sufficiently far that practical testing would be desirable.

The following are agents which can be considered for these sprayings, so far as we can judge at this moment:

Combination of a specially-prepared white oil emulsion with California liquor; a fungicide based on phenolthiazone for fruit trees; a few contact insecticides and feeding poison, which have come forth in large laboratory investigations; and a few leaf lice-combatting preparations (which can only be tested by means of practical experiments).

The result of these sprayings and spraying which will be carried out in the winter with red spider with various emulsions are to be controlled regularly. Further harvest analyses will be carried out for cases that are to be considered in this respect.

Amsterdam, June 17, 1944, 916-K-7651 concerning number 0/1900/0040.

Translated Oct. 24, 1946 - Rochelle H. Bondy
Checked Dec. 2, 1946 - CCM

The Texas Company

TOM REEL 79, BAG 3996, DOCUMENT 126

PREPARATION OF PROPANE PEROXIDE IN A SEMITECHNICAL EXPERIMENTAL PLANT

Through oxidation of propane with oxygen under suitable conditions, one obtains a liquid reaction product, which is denoted by the name "propane peroxide" and which consists chiefly of a mixture of water, hydrogen peroxide and oxy-alkyl-peroxides. These oxy-alkyl-peroxides are formed by condensation of reaction products built up from the original (primary) aldehydes (chiefly formaldehyde) and hydrogen peroxide:

$$CHOH + H_2O_2 \longrightarrow CH_2OHOOH$$

$$2CHOH + H_2O_2 \longrightarrow CH_2OHOOCH_2OH$$

Consequently, the amount of free hydrogen peroxide in the reaction product is dependent upon the ratio between the amounts of aldehyde and of hydrogen peroxide.

Under the optimum reaction conditions (temp. 465°C., contact time 5 sec.) the free hydrogen content (hydrogen peroxide content?) in the solution amounts to about 60 mol per cent of the total amount of peroxides.

Directions for the practical carrying out of these procedures are put down in the following patent specifications:

1. Holl. Pat. #52521

Procedure for the preparation of peroxides by incomplete combustion of hydrocarbons (application April 10, 1940, granted Dec. 15, 1941).

Patent claims:

1. The process of preparation of peroxides by incomplete combustion of hydrocarbons, characterized in this way, that the wall of the chamber in which the combustion takes place consists of non-oxidized metal and that the wall temperature does not exceed 200°C.

2. The process according to Claim 1, characterized in this way, that a reactor of large volume in comparison to its surface, for example, a spherical reactor, is used.

3. The process according to Claim 1, characterized in this way, that the gas flows along the wall of the reaction vessel while one reacts it inside the vessel.

4. The process according to Claim 1, characterized by this, that reaction products are quickly removed and cooled.

2. Holland Patent #52522

Procedure for preparation of hydrogen peroxide by incomplete combustion of gaseous, saturated hydrocarbons with two or more carbon atoms (application April 10, 1940, granted Dec. 15, 1941).

Patent claims:

1. Process for preparation of hydrogen peroxide, characterized by the fact that gaseous, saturated hydrocarbons having two or more carbon atoms per molecule are incompletely burnt with oxygen at a temperature between 440 and 500°C., where the volumetric proportion between hydrocarbons and oxygen is at least 4:1, preferably 7:1 or more.

2. The process according to Claim 1, characterized

by the fact that the primary reaction products are cooled, depending upon the pressure, to such a point that the desired hydrogen peroxide goes over into liquid form and other reaction products, such as formaldehyde and acetaldehyde, remain in vapor form.

3. Holl. Patent #55114

Process for preparation of hydrogen peroxide through incomplete combustion of gaseous hydrocarbons through fractional distillation after removal or conversion of organic peroxides also present (application August 5, 1941, granted March 15, 1943).

Patent claims:

1. Process for preparation of hydrogen peroxide by incomplete combustion reaction products from gaseous hydrocarbons, characterized by the fact that the hydrogen peroxide is recovered by fractionation, after which the organic peroxides also present are removed or converted.

2. Process according to Claim 1, characterized by the fact that the organic peroxides are removed by conversion in acid, after which the products of incomplete combustion are heated once, preferably to a temperature between 40 and 100°C.

3. Procedure according to Claims 1 or 2, characterized by this, that the fractional distillation is so undertaken that a mixture of water and acid is taken from the top of a first rectifier and hydrogen peroxide remains in the bottoms, the overhead mixture being taken over into a second rectifier, about in the center --- can't read this section - has something to do with recovery and reuse of acid by means of a second rectifier.

Method of Procedure and Description of Design of the Semitechnical Apparatus

A mixture of 12.7 m^3/hr. of pure propane (1) and 4.8 m^3/hr. oxygen (3) are led into a reaction vessel (2) through a reducing valve and a metering device. In an emergency, nitrogen (4) can be led into the reactor in place of oxygen.

Because a large wall surface promotes the decomposition of peroxides formed in the reaction, the reaction vessel is spherical in order to have the smallest possible surface/volume ratio.

In order to avoid decomposition of the propane peroxide the reaction vessel (Pat. #52521) is lined inside with V_2A-steel and is equipped with an air cooled jacket which is allowed to cool the reactor wall to a temperature above the dew point of the reaction product.

The propane-oxygen mixture is led into the sphere through an annular opening of such a type that it (the gas) streams along the wall toward the bottom and has a rotary (swirling) motion.

To start the reaction, the gas mixture is ignited by a spark plug. After the reaction has started, artificial ignition is no longer necessary. The reaction temperature is regulated by variation of the oxygen content of the incoming gases at about 465°C. Probably the required percentage of O_2 is less than that given in ~~the scheme (attached sketch, showing amounts).~~

The gaseous reaction mixture is led out through tube (6) where it is cooled only so far that water formed in the reaction is above its dew point - then to a cooler (7) where it is cooled to about 35°C. At this temperature a considerable amount of aldehydes (acetaldehyde) remains in the gas phase, so that the free hydrogen peroxide content in the liquid reaction product is greater than if one cooled to a lower temperature.

The liquid reaction mixture passes out of the cooler into a second ice-cooler (8) where it is cooled to 0°C., in order to stop undesirable decomposition, and is collected in reservoir (9). One makes about 1.5 liters per hour of peroxide liquid with an active oxygen content of about 18 mg. equivalents per cm^3. Of this 18 millequiv., about 10 millequiv. are hydrogen peroxide and 8 millequiv. are oxy-alkyl-peroxides.

In order to isolate the hydrogen peroxide from this solution by means of a rectifying column (not shown in the attached diagram) the organic peroxides are selectively converted into formic (acetic) acid and hydrogen as follows:

$$CH_2OHOOCH_2OH \longrightarrow 2COOH + H_2$$

while the hydrogen peroxide is practically unaffected.

By rectification with steam an azeotrope having 30% H_2O_2 and formic (or acetic) acid is obtained.

The non-condensible gas (16.3 m^3/hr.) emerging from the cooler (7) has the following composition:

CO_2 - 0.6%
C_3H_6 - 8.8
O_2 - 3.2
CO - 3.2
H_2 - 0.1
C_3H_8 - 84.3

This gas is freed of propylene by means of sulfuric acid and is passed through the reaction chamber (2) again by the circulating pump (10).

Yield Without Circulation (Yield per Pass)

The above scheme formed 1.5 l./hr. propane peroxide from 12.7 m^3/hr. of propane; about 12 l./hr. from 100 m^3/hr. (sp. gr. 1.1).

With a content of 10 mg. equiv. H_2O_2/cm^3 and a rectification yield of about 70% one can obtain from 100 m^3 of propane charged:

$$\frac{12 \times 1.1 \times 0.7 \times 10 \times 17}{1000} = 1.58 \text{ kg. of } 100\%\ H_2O_2,$$

corresponding to 5.2 kg. 30% H_2O_2.

Since the reaction product contains about 0.6 mol aldehyde per mol peroxide, of which about 70% can be converted into acid, one can obtain from charging 100 m^3 propane an acid yield of

$$\frac{12 \times 1.1 \times 0.6 \times 9 \times 0.7 \times 50}{1000} = 2.5 \text{ kg. formic acid}$$

(and acetic acid). (The molecular weight of the mixture of formic and acetic acids is taken as 50.)

The yield of hydrogen peroxide with circulation of the reaction gas can only be obtained after concluding the semi-technical studies.

Laboratory of
N.V. de Bataafsche Petroleum Mij.
Prof. Zerbe

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