

SIZING OF PAPER

Dr. H. J. Tadema

May 1943

Frames 2717-2720

Abstract

Research Topics: General Orientation

I. Machine Tests

Since the set-up mentioned in the preceding report (in which the cellulose was sized with 1 per cent Firnagral SO_2 -concentrate) gave results comparable to those produced with colophony (rosin), further tests were undertaken using 2 per cent of these concentrates with the object of obtaining a still higher water repellency.

The sizing was again carried out in hollenders. To the fiber pulp (in approx. 3 per cent concentration) were added successively: concentrated emulsion of Firnagral concentrate, aluminum sulfate solution and sulfuric acid to a pH of 4.5. A second receiver was added in which the sized pulp could be diluted to 1 per cent, the concentration required for the operation of the machine.

The paper obtained showed no noticeable defect, but the amount of sizing was less than expected. In spite of a content of 1.8 per cent concentrate, the water permeability based on 100 grams per square meter amounted to only 70-80 seconds, against 100 seconds by the previous experiment (0.9 per cent concentrate). It had been necessary to prepare the cellulose slurry a day ahead of time, and the long standing of the sized, diluted suspension probably caused the adverse influence on the sizing.

Previously, three products had been used in Lubex sizings:

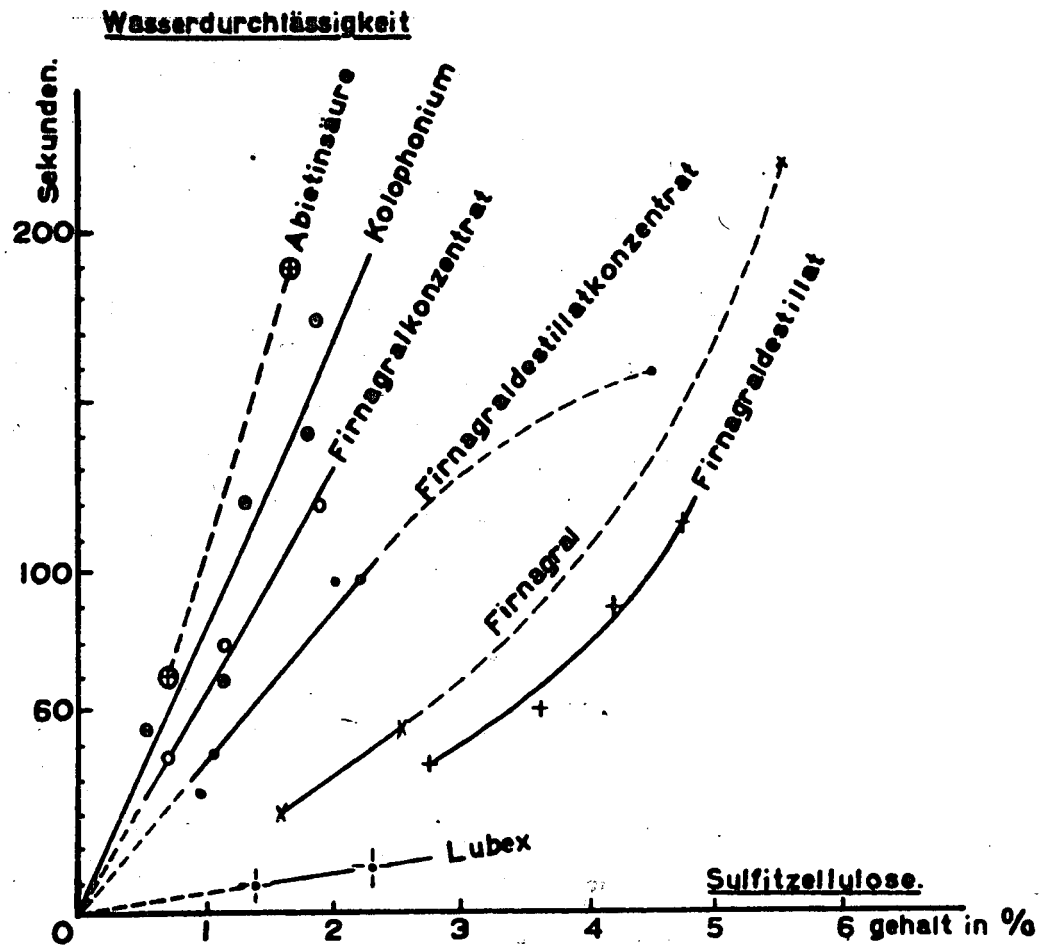
Firnagral (TMC 9863, TL 7011)

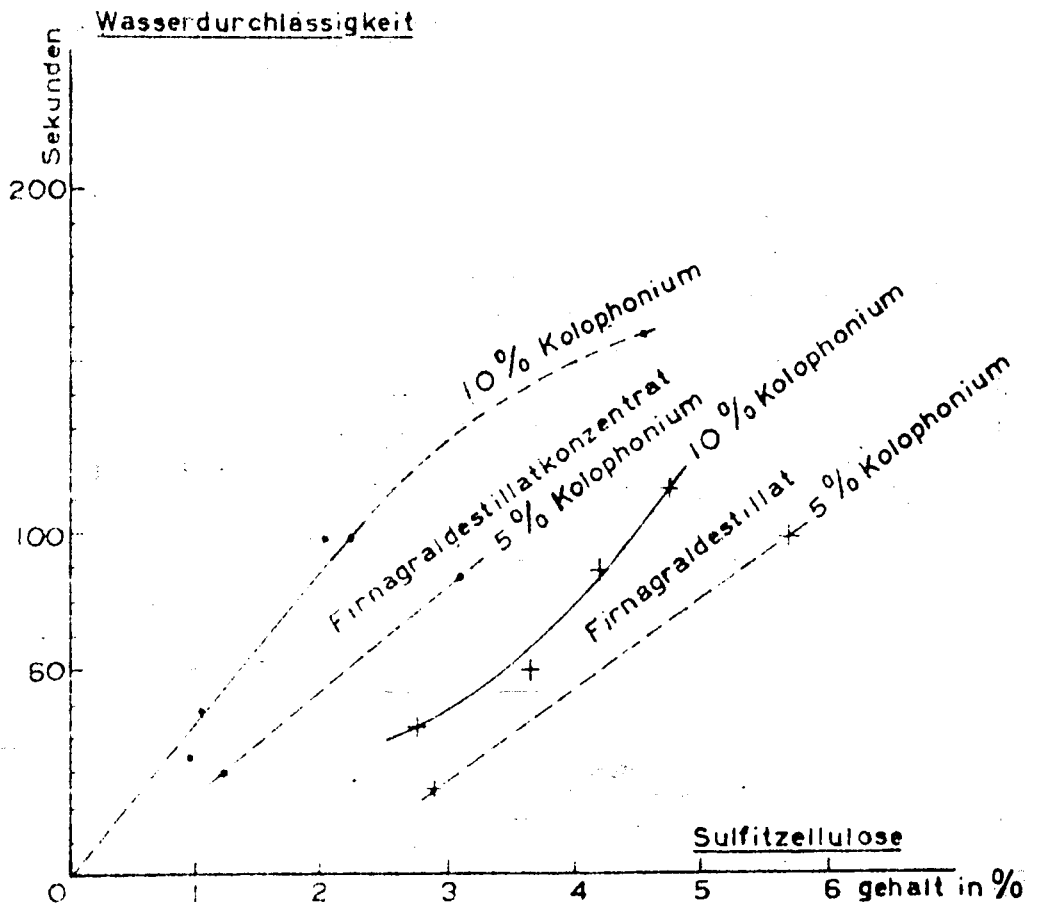
Lubex (TMC 447, TL 7588)

Distillate from heavy Lubex (TMC 59, TL 7220)

The last named product is a distillate of Firnagral, and hereafter in these reports is called Firnagral distillate. SO_2 -concentrates are made by combining Firnagral and Firnagral-distillate.

Similar products were tested in various concentrations on a bleached cellulose sulfite. Rosin and abietic acid were run as control materials. The three unconcentrated products were emulsified with 10 per cent rosin, as was the Firnagral distillate. The concentrate of





Firnagral formed a good emulsion of 20 per cent rosin. From the results obtained (Diagram 5472-1-B4, attached), the following conclusions were drawn:

- a. The sizing is approximately proportional to the concentration. A sizing factor for the relation between the permeability and concentration can be introduced.
- b. Firnagral sizes better than its distillate, in disagreement with the experience of the Rhomania. Lubex has only limited effectiveness.
- c. The concentrates are much better than the raw products. Firnagral concentrate sizes better than its distillate, due probably to the higher resin content of the Firnagral concentrate emulsion.
- d. The sizing with Firnagral SO_2 -concentrate is almost as good as with rosin.

It can also be discerned from the diagram what blends are necessary to the attainment of a 60-second water-permeability.

SIZING OF PAPER WITH LUBEX AND LUBEX PRODUCTS

Dr. H. J. Tadema

May 1942

Frames 2723-2805

Abstract

Research Topics: General Orientation

INTRODUCTION

The object of the investigation was to determine whether a certain distillate from lubricating oil extract could be used as paper-sizing.

It was hoped to replace the proportionately costly product (rosin) by a very cheap one for which few other applications existed. In 1938 some work along this line was done in Dr. Tadema's laboratory under the auspices of the Rhemania, with little success.

The problem was less simple than it seemed. The following description of the art as it was usually practiced was given:

"The best sizing media is colophony (rosin). This consists principally of abietic acid (an aromatic monocarboxylic acid $C_{20}H_{30}O_2$) or its ester. Resin soap of a gelatinous consistency is manufactured through treatment with concentrated alkali. This resin soap is composed of a concentrated solution of sodium abietate, in which is found the unsaponifiable accessory of resin in solution or in an emulsified state. Through distribution in water, resin-milk, an emulsion or suspension, is made. Upon dilution of the soap, the salt of abietic acid hydrolyzes (this acid is insoluble in water). The resin-milk first is added to the cellulose slurry out of which the paper is manufactured, and $Al_2(SO_4)_3$ solution then is added until the total acidity of 4.5 is reached. Thereby more reactions can take place:

1. Al-ion is adsorbed on the fiber surface.
2. $Al(OH)_3$ or basic $Al_2(SO_4)_3$ precipitates as a gelatinous, strongly adsorbing mass.
3. The resinate still in solution precipitates as an insoluble aluminum salt. (The resinic acid emulsion particles bind to the Al-ion on the fibers.)

There are two ways in which the resin binds itself to the fibers:

through adsorption of Al-resinate on the fiber surface, and through encasement of the emulsion particles with flocculant $Al(OH)_3$. If other agents than rosin are used, adsorption takes place in one of these ways. Lignite wax (principally montanic acid, aliphatic monocarboxylic C_{23}), casein (in alkaline solution) and water glass probably are bound through adsorption to Al-ion. A sharp separation therefore is not possible.

With regard to the strong flaking-out method of precipitating resin, practically only Al-ion is suitable. Ca- or Mg-ions must be used in far greater concentration.

Since as many things could be done with extract of lubricating oil, with other types of molecules, as with rosin and lignite wax, that is to say, with hydrocarbons, then the solution of the problem could be pursued along two basically different lines.

On one hand, the most "glutinative" hydrocarbon molecules could be investigated in an effort to procure a sizing which would be analogous in some measure to gelatin, etc., should a suitable sizing not be forthcoming through precipitation of a resinic acid-aluminum salt.

On the other hand, Lubex might be chemically altered in such a way as to obtain a substance possessing acid groups, and in this respect similar in some degree to the natural resin.

The problem was to be approached from both angles in Dr. Tadema's investigation. After making an extensive study of the literature on the subject for the purpose of orientation, it was planned first to follow the action of the ordinary sizing microscopically, since knowledge of the nature of the arrest on the fiber of the ordinary "good" resin or gelatin sizing (whether it shut off the capillaries or whether it covered the surface of the fibers) would give some criteria for judging the results of sizing with Lubex.

MICROSCOPIC EXAMINATION

The following set-up for the microscopic examination proved best: Lighting with arc lamps, ordinary glass condensers, filter cups filled with $CuSO_4$ solution, filters of ultra-violet penetrable glass (from analytical lamps), ordinary microscope condensers (set at unity, with water drops between condenser and objective). An Euphosfilter was placed around the stage to eliminate ultra-violet light. It was found that fibers could be made more visible with the florescent dyestuff, preferably Geranium G. 2727

The first microscopic examination was not held conclusive, because the cellulose base used had stood for a long time in water and probably had deteriorated. The impression was obtained that the resin particles lose themselves between the separate fibers, and collect most thickly on the surface of the paper.

INTRODUCTION OF ACID GROUPS IN LUBEX

The object of this work was to ascertain whether a useful product could be obtained through the introduction of an SO_3H -group, which is much simpler to effect than that of the COOH -radical. Since sulfo-acids possess strong acid properties (dissociation constant of approx. 0.2), it was not expected to obtain good flocking-out with Al -ion. It was hoped to find a form intermediate in this respect in a combination of phosphoric and arsenic acids, which would have a dissociation constant of 10^{-2} to 10^{-3} , or possibly in a combination of boric and silicic acids.

The sulfonation of Lubex, on account of the aromatic constituents, had to be carried out under very mild conditions so as to avoid repeated sulfonation.

JUNE 1942

To the procurement of a good sizing, it was necessary to add at least 2 1/2 per cent resin (calculated on the amount of the cellulose material) to the water-diluted paper slurry. It was found that the 1 per cent resin already present in the unsized paper exerted no influence on its sizing property.

The sulfonation of Lubex with acids of sulfur in concentrations of 50 per cent or less gave at room temperature no satisfactory amount of oil-soluble sulfonic acids.

JULY 1942

It was found that Lubex actually could be well emulsified, using colophony (rosin) as the emulsifier. The emulsions obtained were very stable, of particle size less than 1 micron. De-oiled Lubex could be emulsified in the same manner, but less completely.

It was possible to size paper with the Lubex emulsions. However,

1. the savings on colophony were not great;
2. the high oil content of the paper gave to it so displeasing a color and poor texture that it was practically unserviceable; and
3. the mechanical properties were considerably worse than with unsized paper.

While the quest for emulsification of Lubex was at this point regarded as lost, it came to light during these tests that a good emulsification was not synonymous with the best sizing agency. The adherence of the particles of the emulsion to the fiber of the paper, and the wetting of the fiber surface by the oil also were found to be critical with regard to the full action of the sizing agent.

An analytical scheme was worked out for the determination of colophony in emulsions.

AUGUST 1942

A stable emulsion was be produced from 80₂ de-oiled Lubex after fusion with 10 per cent colophony. Sizing tests with this concentrate gave excellent results; it was found to size much better than Lubex and equally as well as colophony.

Benzoic and palmitic acids, dissolved as sodium salts and precipitated with aluminum sulfate, on the whole, showed no sizing agency.

Further testing of paper sized with Lubex emulsion brought to light that drying at room temperature offered the possibility of carrying out through extraction an analysis of the emulsion particles on the fibers. Drying too long at higher temperatures injured the sizing (because of steaming and oxidation of the sizing material).

It was attempted to analyze synthetic colophony-Lubex mixtures by means of refractive index, but the coloring of the material was too dark to permit accurate determinations. The determination of acid number was still regarded as the best method.

SEPTEMBER 1942

Through a brief hydrogenation of Lubex distillate, an important improvement of the color was obtained. The green fluorescent product was markedly less viscous than the original product, and gave an extinction coef. of 0.20, much lower than that of the distillate itself.

Up until this time sizing emulsions were always prepared from Lubex (TMC 59) or a product from Lubex. Now experiments were run with Firmagral (TMC 868). Lubex is a distillate of the total 80₂-extract from which the lightest fraction and the residue have been removed. In Firmagral these components are still present. Dr. Tadema believed that the difference in the two lay in the presence in Firmagral of the residue; the color from Firmagral was darker than that from the distillate, and Firmagral gave an extinction coef. of 2.70, whereas Lubex gave 0.89.

It was endeavored to decrease the dye intensity and at the same time to retain the sizing quality of the Lubex distillate. (Papers sized with the material always came out yellow to brown.) To that purpose, it was found that treatment with Ferrana in benzene solution gave a marked improvement (Extinction coef. with no treatment, 0.89; upon treatment with the Ferrana-benzene, 0.47.)

OCTOBER-NOVEMBER 1942

By measurement of the intermediate particle size of a number of strong emulsions it was discerned that the particle size of a very stable emulsion should be less than 0.2 micron.

In testing to determine the best emulsification conditions it was found that:

- a. the lye concentration should be about 10 per cent.
- b. a total saponification gave the best product.

- c. a colophony content of about 5 per cent gave a very fine emulsion, and that 2 per cent was not sufficient to hold the emulsification;
- d. longer and stronger stirring during the addition of the lye yielded an emulsion stable even in a concentration of 50 per cent.

DECEMBER 1942

Further emulsification tests were conducted on Firmagral, varying the concentrations of alkali and of rosin. NaOH and NH₄OH (in solutions of normality approximately equal to a 10 per cent KOH solution) gave equally stable Firmagral emulsions with 5 per cent rosin as did KOH. However, the particle size was smaller when KOH was used.

Experimenting was done with the SO₂-concentrate of Firmagral using rosin, tall oil, lignite wax, sodium sulfonates A and B, sulfonate of AX-distillate and ester salts as emulsifying agents, showing:

- a. that very good emulsions could be obtained with 20-30 per cent colophony-KOH;
- b. that emulsification with sulfonate A was possible;
- c. that tall oil might possibly serve as a substitute for colophony.

It further came forth that the emulsification could be simplified by stirring during the dispersion and not, as was previously done, until the end. The additional pouring out of the very concentrated oil-in-water emulsion into water of the same temperature was omitted, thus avoiding the annoying appearance of lathers.

Sizing tests with a raw material easier to size, namely, cellulose sulfate (cellulose treated by the soda method) were carried out on a laboratory scale; emulsions of Firmagral concentrate in many runs were equal to colophony emulsions.

It was discovered that sizing with the finest portion of a Firmagral concentrate emulsion was not as good as that obtained using the whole emulsion.

JANUARY 1943

Firmagral was separated into a number of fractions by steam vacuum-distillation. The second, fourth and sixth fractions as well as the residue, were treated to the concentration of the aromatic portion and afterward were emulsified. The fractions, which at the beginning exhibited a bright color, became darker on oxidation in air.

Emulsification tests showed that the higher fractions gave coarser emulsions; the emulsion of the residue was also very unstable.

Better emulsification was obtained by first concentrating the fractions. The emulsions from the concentrates were gray in color.

The sizing properties were better the heavier the fraction. The lower fractions (up to about 50 per cent distillate) gave worse sizing than did the original Firmagral; the higher fractions (50-75 per cent distillate) sized about twice as well as the Firmagral and gave a better color. The residue gave by far the best sizing (about 5 times as good as Firmagral) but imparted a very dark color to the paper.

In summary, the concentrates of the fractions sized better than the fractions in their original state; the concentrated residue sized considerably worse.

By comparison of the better sizing effects through concentration with SO_2 on one hand and those obtained with the fractionated distillates of Firmagral on the other, it was shown that the sizing factor in the first case was lower; however, it was believed that these figures could be raised through a better SO_2 concentration. (See Diagram No. 5708-1-B4, Attached.) Combination of both methods, so as to first distill and then concentrate, led to inferior results staggering cost and greater trouble.

Exemplary data obtained in these experiments:

In cellulose paper prepared by the soda method sized directly with Firmagral, a concentration of 2.75 per cent brought a size-fast time (water-permeability) of 60 seconds. That is to say, with 1 kilogram of this Lubex, 36 kilograms of paper could be sized. For the SO_2 -concentrate of Firmagral, the concentration necessary to the attainment of 60-second water-permeability was 0.94 per cent, corresponding to 106 kilograms of paper per kilogram of concentrate.

Precipitation experiments with Firmagral emulsion showed that a poor sizing and a high aluminum content usually went together; this phenomena did not hold with colophony sizing. (See Table I, Attached.)

It was undertaken to chemically treat (introduce acid groups) Lubex and to determine the effect on its sizing agency. A control material of approximately the same C and H content (Tetralin) was run parallel with the complex product Lubex. In the first set-up, the concentration was carried out with phthalic anhydride in the presence of AlCl_3 . This treatment caused the oil to emulsify and also improved the sizing.

FEBRUARY 1943

Success was obtained in producing a sufficiently-sized paper with Firmagral SO_2 -concentrate, the mechanical properties of which were not poorer than paper sized with colophony or unsized paper. The amount of sizing was about $\frac{2}{3}$ that with colophony. (Details of the process: Kraft cellulose and Firmagral SO_2 -concentrate were used as raw materials. One per cent oil was mixed with the dry fiber. The concentrated slurry was sized in a hollander, and 25 grams of $\text{Al}_2(\text{SO}_4)_3$ per kilogram of fiber were added, so that the aluminum content of the paper was held to a maximum of 25 per

cent. The pH of the slurry, which after the addition of the emulsion reached 7-7.5, became 5-5.5 with this amount of $\text{Al}_2(\text{SO}_4)_3$. A little H_2SO_4 was added in order to bring the pH to the usual value of 4.5. The back water was also brought to this pH, and the improvement in the sizing was noticeable. The pH of the backwater soon rose to 0.5 higher than that of the fiber slurry. Slight variation of the pH indicated the optimum conditions to be: pH of the slurry = 4.4; pH of the back water = 4.8-5.0.)

On heating Firmagral in air with KOH, a hard, black mass with an increased acid number and saponification number was obtained. A combination of this product and untreated Firmagral emulsified easily and gave a good sizing.

Attempted reaction of Firmagral with KHCO_3 or NaHCO_3 in an open crucible did not succeed because the bicarbonates decomposed.

Orientation experiments were made toward reaction of Na-sulfonate with $\text{K}_4\text{Fe}(\text{CN})_6$, K-formate and KOH; only with the KOH did any reaction take place.

MARCH 1943

A machine test was carried out, in which 1.8 per cent Firmagral SO_2 -concentrate was used as sizing (0.9 per cent was used in previous tests). The water-permeability was not improved thereby, but was diminished. (However, it was thought that this may have been due to the fact that the supply of fiber slurry had stood too long.)

The results of previous experiments with the handsieve were compiled in Diagram No. 5742-1-B4 (Attached). These results showed that:

- a. The sizing corresponded closely to the concentration of sizing material;
- b. Firmagral sized better than its distillate;
- c. The original concentrates sized better than their products;
- d. Sizing with Firmagral SO_2 -concentrate was equal to that with colophony.

From a second diagram (5742-2-B4, Attached), concerning the influence of the rosin (colophony) concentration on the sizing with Firmagral distillate and on that with Firmagral SO_2 -concentrate, respectively, it can be seen that the improvement by increasing the colophony concentration did not entirely correspond to that by increasing the resin concentration.

Heating Firmagral with KHCO_3 in an autoclave produced no reaction.

Chlorination of Firmagral at 10 C with AlCl_3 as catalyst yielded a compact, solid product which, emulsified with 10 per cent rosin, gave a good sizing. Chlorination without catalyst at 100-120 C gave a partially-

chlorinated product hard to emulsify and which gave a poor sizing.

Unsuccessful results followed attempts to substitute chlorine in a cyano-group in the products obtained, and to saponify the resulting nitrile.

APRIL 1945

The sizing agency of Firmagral on kraft cellulose was noticeably improved by increasing the rosin content.

In tests with extracts acquired by washing Firmagral in SO₂ with benzene, it was shown that better water-permeability resulted accordingly as the Lubex was further extracted. (The SO₂ solution of the Lubex was agitated in countercurrent with benzene in a stepwise series of five separatory funnels.)

The residue from a steam distillation of Firmagral and heavy Lubex proved a better sizing agent than rosin. The highest-boiling cut from Firmagral also sized well; the corresponding fraction of the heavy Lubex was much less active.

Tests on unbleached cellulose sulfite, steamed mechanical wood and a blend of both, using rosin, Firmagral concentrate and the residue from distillation of Firmagral gave sizing equal in quality and quantity to that obtained earlier using these materials on bleached cellulose sulfite and kraft cellulose.

Attempts to substitute acid groups into Firmagral through reaction with phosgene were unsuccessful.

Voltolized Firmagral was easily emulsified and had good sizing properties. (Standard Firmagral was voltolized, whereby the viscosity was considerably increased and the color became more red.) Used on bleached cellulose sulfite, 2.7 per cent (added) or a 1.9 per cent concentration, of this standard product was necessary to the attainment of a 60-second water permeability. The concentrated fraction, 20/21, gave 2.4 per cent (added) or 1.2 per cent concentration.

MAY 1945

A machine test proved that better sizing was obtained with a freshly sized base (kraft cellulose + 10 per cent steamed mechanical wood; 2 per cent Firmagral concentrate) than with a sized paper slurry which had stood for some time.

Tests with the handsieve using kraft cellulose as the raw material showed that the water-permeability with colophony, as well as with Firmagral concentrate, in the beginning rose sharply, and after that increased in limited amounts as the concentration was increased. Colophony gave higher values than Firmagral for low concentrations, whereas in higher concentrations (greater than 2 per cent) the reverse was true. (See Diagram No. 5778-B4, Attached.)

JUNE 1943

In investigation of a new type of colophony, a settling of the dispersed particles often occurred upon emulsification of Firnagral SO_2 -concentrate and Firnagral distillate. It was not known whether this was due to the type of colophony used.

A machine test was run to see whether Lubex was useful to the sizing of old paper. As raw material, a 1:2 mixture of old paper and a hard-to-size cellulose sulfite was chosen. Good sizing with Lubex resulted, but the mechanical properties of the paper were poor. This was believed due to the irregular structure of the paper. Further tests were to be conducted.

Voltolization of a mixture of Firnagral & 20 per cent colophony gave a product which produced somewhat better sizing than did voltolized Firnagral alone. Since their sizing effect was considerably less than that of Firnagral SO_2 -concentrate, these costly voltolized products were not considered practical for use as paper sizing. (The products had stable boiling points and were somewhat brittle. It was thought that other uses might possibly exist.)

JULY 1943

Firnagral distillate in a concentration of 2 per cent gave sufficient sizing (equal to that with 1 per cent colophony) on bleached cellulose sulfite. The paper, however, had a yellow color which lessened its usefulness as writing paper.

From his experience thus far, Dr. Tadema recommended Firnagral as the best sizing for easily-sized, evenly-colored raw materials such as kraft cellulose and steamed mechanical wood.

Further emulsification tests with the residue from distillation of Firnagral showed that the success of the emulsification

- a. was independent of the type of colophony used;
- b. in some degree was influenced by the temperature;
- c. was heavily dependent upon the lye concentration, the necessary concentration lying around 10 per cent or higher KOH;
- d. was influenced by the speed of the addition of lye and water, and by the temperature during the course of the addition;

A good emulsification of the product possessed a notably green color and very small particles.

AUGUST 1943

Further tests using Lubex sizing on old paper indicated that the sizing itself gave no noteworthy decline in the mechanical qualities of the

paper.

In other laboratory tests upon the residue from distillation of Lubex, it became evident that:

- a. to the attainment of an emulsion of small particle size, the velocity of stirring during the dispersion of the lye in the oil-resin mixture (first emulsion phase) and not the stirring during mixing of the resulting oil emulsion with water (second phase) was important;
- b. a coarser emulsion resulted through pouring out the paste obtained in the first phase into water than by adding the water to the paste;
- c. to obtain the best result, the temperature, in the first phase as well as in the second, had to be held within narrow limits;
- d. although NaOH gave poorer emulsification than KOH, it might possibly be used in the technical application; and
- e. addition of 2 per cent of lignite wax gave a very stable emulsion of a smaller particle size.

Sizing tests with emulsions of the residue from distillation of Firnagral showed that variation of the separate particle size between the limits 75-400 millimicrons had no effect on the sizing action.

It was also found that the cause of coarse dispersion often could be traced to the clumping-together of small particles in emulsions with a concentration greater than 10 per cent. It was possible to avoid this clumping-together by the addition of a small amount of a weak acid, such as resenic acid, boric acid or carbonic acid.

SEPTEMBER 1943

When more KOH than colophony was added to the resin-Lubex mixture to be emulsified, coarser emulsions resulted than with incomplete saponification. Moreover, the emulsions were less stable because of the excessively high pH.

Ninety per cent saponification was recommended for technical processes. Adjustment of the pH to 8.9 through addition of gaseous CO_2 was found to increase the stability of the emulsions obtained. For this purpose, it was found necessary to add somewhat less CO_2 than was calculated for conversion of all the KOH to K_2CO_3 .

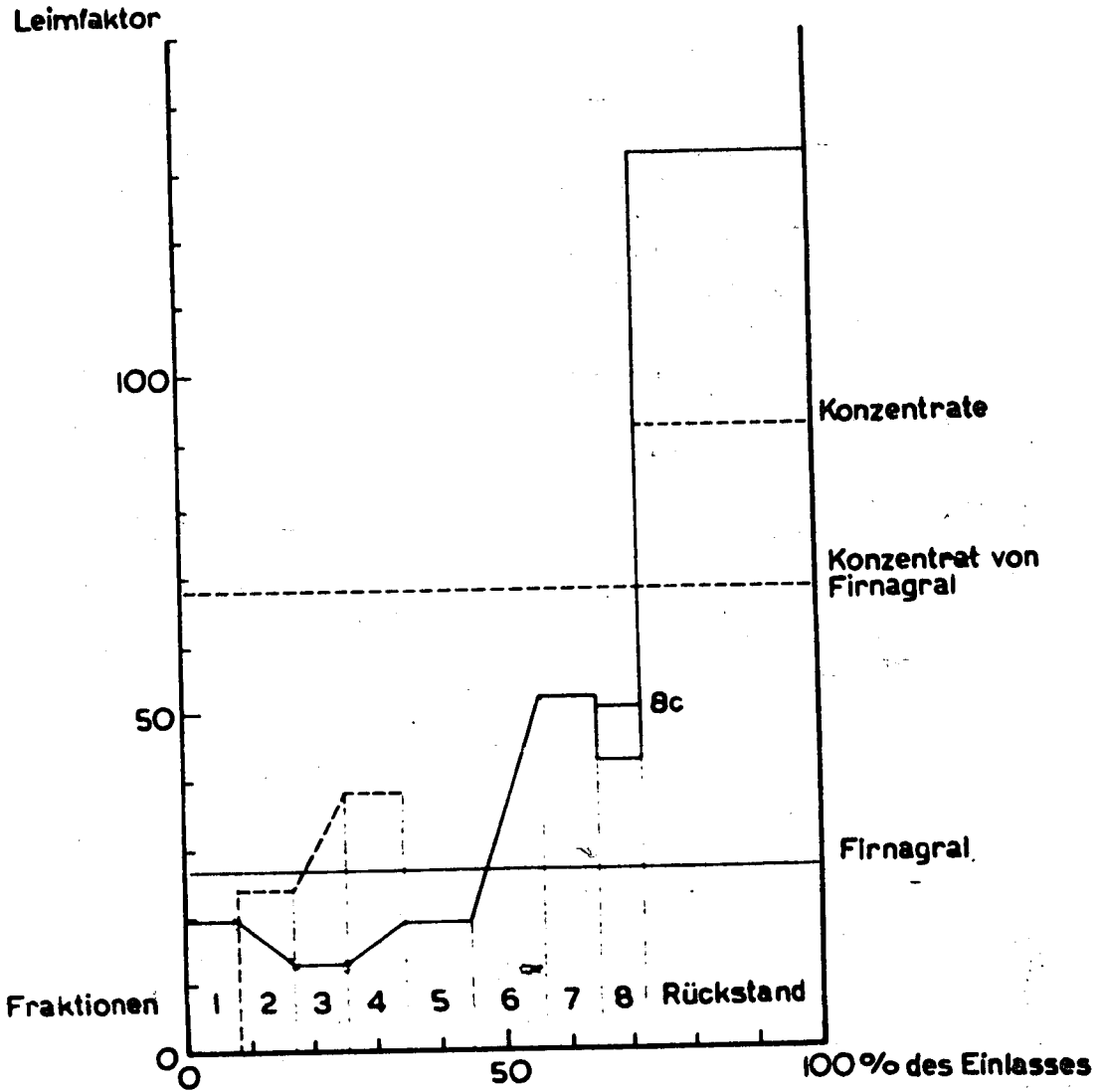
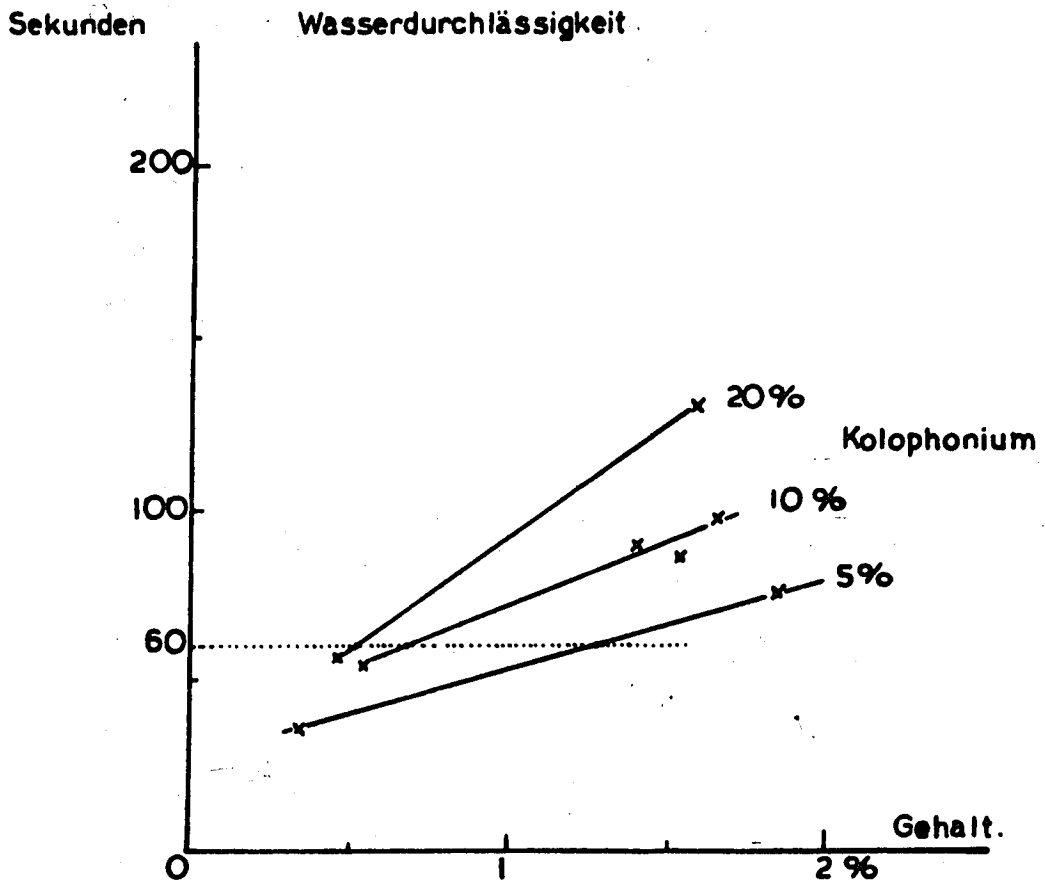


Table I

Exp. No.	Description	Water Permeability Sec. for 100 g./sq.m.	Oil Content, Average %	Sizing Factor
BH	Precipitation with $Al_2(SO_4)_3$ to pH = 4.5	107	0.76	148
BH 5	Same as BH	72	0.56	128
BH 6	Same as BH, but removed under vacuum	112	0.62	180
BH ¹	Same as BH	48-90	0.55	88-164
BL	First extra. KOH, after that precipitation with Al to pH = 6.5	102	0.85	120
BJ	Precipitation with Al to pH = 4.5, after that KOH to pH = 6.5	95	0.71	134
BH 4	Precipitation with Al to pH = 4.5 diluted with back water from the machine	104	0.67	155
BI	Precipitation with H_2SO_4 to pH = 4.5	81	0.53	153
BI ²	First extra. KOH, after that precipitation with H_2SO_4 to pH = 6.5	3	0.04	75
BK	Precipitation with H_2SO_4 to pH = 4.5, after that KOH to pH = 6.5	12	0.36	33
BK ¹	Check on BK	6-40	0.20	35-270
BE 1	Precipitation with $Al_2(SO_4)_3$ to pH = 6.5 diluted with distilled water.	94	0.6	158
BE 2	Same, diluted with water brought to pH = 6.5 with Al	47	0.6	78
BE 3	Same, diluted with dilute H_2SO_4 to pH = 6.5	99	0.6	157



Sekunden Wasserdurchlässigkeit.

