Report 9261

# SIZING OF PAPER WITH LUBEX (EDELEANU OR $SO_2$ EXTRACT OF LUBE OIL)

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## Abstract

The purpose of the investigation was to determine how rosin can be replaced by the Edeleanu (sulfur dioxide) extract of lubricating oil for use in sizing paper. From earlier experiments it was known that Lubex, especially if it was emulsified with rosin, possessed sizing properties. A good method for the emulsification of Lubex was sought. Tests were then made to determine which Edeleanu extract is best and how this can be improved. The sizing effect of the emulsions obtained was examined on a laboratory scale and on a semi-works scale using various small paper machines. The influence of the type of paper base used was also exhaustively investigated. Other emulsifying agents than rosin were studied, but the results were unfavorable for all but rosin. The structure of rosin and Lubex was compared and an attempt was made to introduce organic acid radicals into the polynuclear aromatic compounds of Lubex to make acids corresponding to those of rosin. Although useful products were obtained, it was believed that the conversion process was too expensive for practical use.

The Edeleanu extract was obtained from the multi-stage extraction of heavy lubricating oil with sulfur dioxide dissolved in naphtha. The concentrate thus obtained was melted together with twenty per cent by weight of rosin with good stirring. While still warm the mixture was poured into an emulsification apparatus and mixed with vigorous agitation at 60 C with a 20 per cent potassium hydroxide solution, with saponification of 90 per cent of the Lubex and rosin. The water-in-oil paste obtained was cooled to 40 C and then further diluted with water until an emulsion containing a maximum of 40 per cent of oil in water was obtained. The resulting emulsion could be used to size steamed wood pulp or sodium kraft cellulose, using about 1 per cent of the sizing. The sizing is precipitated with not more than 25 g. of aluminum sulfate per kilogram of dry material and finally by adding sulfuric acid until a pH of 4.5 is reached.

Rosin from various sources was found to be equally effective for producing emulsions for use in sizing. At least 5 per cent by weight of rosin in Edeleanu extract was necessary for satisfactory use of the latter for sizing. Use of more rosin made the emulsification easier and the sizing better but not in direct proportion to the rosin content. Potassium, sodium and ammonium hydroxides were satisfactory for producing

Lubex-rosin emulsions. Potassium and sodium carbonate could be used for rosin alone but not for Lubex-rosin mixtures. The concentration of the caustic is one of the most important factors in the emulsification, 10-20 per cent by weight of potassium hydroxide being required. It was reported that sufficient caustic to saponify the rosin completely was the most favorable; excess caustic caused unstable emulsions to be formed Therefore, they recommend adding sufficient caustic to saponify 90 per cent of the rosin. If excess caustic is used, they recommend adding sufficient weak acid or carbon dioxide to neutralize part of the caustic and stabilize the emulsion. They recommend vigorous stirring of the Lubex-rosin, oil and caustic solution (which is slowly added) to produce a water-in-oil emulsion of very fine particle size first, followed by addition of water, wherein the stirring is not so important, to produce the oil-in-water emulsion required for sizing. The temperature at which this emulsification is effected is important. A temperature of 60 C is recommended for the first stage; above this temperature, the emulsions are unstable because the oil is so fluid that it tends to flow together again, while below this temperature emulsification is not attained rapidly enough. The emulsion is then cooled to 40 C for the second stage of the emulsification and water is slowly added with moderate stirring, as a result of which the temperature may drop still further without harm. The emulsion is ordinarily precipitated upon the paper pulp with aluminum sulfate. The pH of the diluted fiber pulp is adjusted to 4.5-6 before adding the aluminum sulfate. In the machine tests made at Amsterdam with rotary screens, difficulty was encountered with kraft paper if the pH was below six because of thin round places appearing in the paper, resulting from air bubbles clinging to the screen or also from rosin separating out and making greasy spots on the screen. With bleached sulfite cellulose, a pH of 4.5 could be used satisfactorily with the machines. At a pH of six or above difficulty was encountered in precipitating the emulsion. This difficulty was overcome by mixing the paper pulp with the required amount of emulsion in the hollander; precipitating with aluminum sulfate (using not more than 25 g. per kilogram of dry material); and finally adjusting the pH to 4.5 by the addition of dilute sulfuric acid to precipitate the emulsion sufficiently. Excess caustic may cause separation of the oil-in-water sizing emulsion into conglomerates which separate from the clear liquid; however, these can be readily dispersed again by stirring. Neutralization of part of the caustic with weak acid or carbon dioxide to a pH of 8-9 or addition of a solution containing several per cent of casein will ordinarily stabilize these emulsions.

The kind of Lubex used has considerable effect upon the sizing effected. Ordinarily, the sizing is better the heavier the Lubex used. One can improve the extract either by distillation or by concentration with sulfur dioxide-naphtha. By the distillation of Firnagral (a Lubex obtained from one oil) it was found that the lightest fractions size worse than the initial material; the middle fractions representing 50-75 per cent of the initial material size better; and the residue sizes by far the best. If the Firnagral is dissolved in sulfur dioxide and washed with naphtha, preferably in several steps, the concentrate obtained likewise sizes much better than the original product. Comparative data for the grades of Lubex are tabulated and also presented in graphs at the end of the report. The sulfur dioxide-naphtha concentration is favored because of the increased amount of fiber which can be treated with a given amount of extract and

because the Lubex is available in the plant in sulfur dioxide solution, ready for the naphtha wash. The Lubex concentrate and distillation residue suffer from the disadvantage that they are dark colored. They can be used for sizing dark colored wrapping paper. If the color of these products was made lighter by treatment, the sizing effect diminished. Only the middle distillation fractions, amounting to 50-75 per cent of the starting product, had a very light color with an increased sizing effect.

The successful use of Lubex for sizing depends upon the kind of paper fibers with which it is to be used. Firnagral can be recommended as a substitute for rosin only with fibers which are easily sized such as sodium kraft cellulose and steamed wood pulp. For small sizing content, the use of rosin is advantageous but at higher sizing content, the concentrate is equivalent. With bleached sulfite cellulose the sizing effect is, in most cases, directly proportional to the sizing content. Bleached sulfite cellulose could be sized satisfactorily with Firnagral concentrate, but for production of light-colored paper, the middle distillation fractions were required. Data showing the effect of the fibers used are presented graphically at the end of the report.

Laboratory scale sizing tests were made first to select promising sizing materials and procedures. The more promising sizing emulsions were tested further with machine tests which were made with a rotary screen machine at the B.P.M. Laboratory in Amsterdam. The most promising of these were tested on the long screen machine in the Laboratory for Technical Botany at Delft. From the results of these machine tests, it was concluded that the mechanical properties of paper sized with Lubex need not be inferior to those obtained with rosin.

From the results of the above tests, it was concluded that the following sizing procedure is the most favorable:

Wash the Edeleanu extract from heavy lubricating oil in sulfur dioxide solution with naphtha in several steps and emulsify the concentrate obtained with rosin and potassium hydroxide as previously described. In case this emulsion should show a tendency to settle because of too strong an alkaline reaction, pass in carbon dioxide to a pH of 8-9. With this emulsion, steamed wood pulp or sodium kraft cellulose can be sized (1 per cent by weight of sizing material). Do not use more than 25 g. of aluminum sulfate per kilogram of dry material for the precipitation; then bring the mass to a pH = 4.5 with sulfuric acid. It is recommended that the sizing be effected in as concentrated a paper pulp as possible; otherwise difficulty is encountered from small lumps or oil droplets. It is best to size immediately in a hollander using a fiber concentration of several per cent. This concentrated mass is very stable; however, after dilution to 1 per cent fiber concentration or less, the sizing failed after several hours in their experiments.

Emulsification with other materials than rosin was investigated. None was as effective as rosin. The best was tall oil (acids recovered from sulfite liquor from paper treating processes), which can be used alone as sizing material. Emulsification with sulfonates was possible, but the emulsions were much coarser than those prepared with Lubex-rosin. With

montan wax, the sulfonate of an acetylene-xylene condensation product, and ester salts, no emulsification was obtained. It was found that a 20 per cent montan wax-to-rosin ratio (4 per cent based upon the Lubex emulsified) gave still better emulsification of the Lubex.

The chemical structure and treatment to produce better emulsions were considered. There is a certain analogy between the structure of rosin and Lubex in that both contain polynuclear aromatic compounds. Rosin consists chiefly of abietic acid or pimaric acid. Lubex contains many polynuclear aromatic compounds but does not contain many organic acid radicals. An attempt was made to modify the structure of Lubex to resemble that of rosin by the introduction of organic acid radicals to see if rosin could be dispensed with in the sizing process. To see if organic acids had the desired effect, it was determined that abietic acid alone is better than rosin for sizing, although the former is crystalline and not resinous. Also, it is known that montan wax sizes well and that this consists of acids with paraffinic chains ($C_{28}$) and their esters. Benzoic acid and palmitic acid, which latter corresponds with the acids of montan wax, had no sizing effect. Tetralin was then condensed with phthalic anhydride, in the presence of aluminum chloride catalyst, to produce a ketonic acid which was reduced to the corresponding acid. Both the ketonic and the reduced acids dissolved in alkali and precipitated upon the fiber successfully, but they produced no sizing effect. This same condensation-reduction reaction was effected with the lowest and highest distillation fractions of Firnagral with results similar to those obtained with tetralin, but the resulting product did produce a sizing effect in this case. Therefore, it was concluded that it is possible to convert Lubex into a kind of rosin by introduction of organic acid radicals, although this procedure is expensive. It was then determined that this same effect could be produced by the oxidation of Lubex with air and potassium hydroxide at elevated temperature. The side chains were decomposed and oxidized to organic acid radicals. The product from Lubex had a high acid number, but could not be brought into solution or emulsion. However, after melting this with Firnagral, this result was possible and the product exhibited good sizing action, which indicates that the oxidation product must be very good. Reactions of Lubex with phosgene, Cl-formic acid ester, and urea chloride were attempted with unsatisfactory results.

Finally, several experimental techniques used in these investigations were described, which are summarized below:

For the measurement of the particle size of the emulsions, the following three techniques, which were described in detail, were used:

| Particle size | Procedure |
|---|---|
| Over 1 $\mu$ | Direct measurement under the microscope. |
| 0.1 to 1 $\mu$ | Counting with the split ultramicroscope. |
| Below 0.1 $\mu$ | Measurement of the light extinction. |

The sizing particles were examined microscopically, but, with

the ordinary microscope, using visible light, the sizing could not be seen on the fibers. However, by using ultraviolet light, the rosin and Lubex fluoresced with a green color and films as thin as 0.1 $\mu$ were visible on the fibers. The slight green fluorescence of the fibers themselves was completely suppressed by dyeing the fibers with geranium pink dye, which fluoresces to give an orange-red color. Therefore, the sizing appeared as green markings upon an orange background. With the use of an Euphos glass filter in the eye piece of an ordinary microscope, this fluorescence could be observed. A carbon arc was used as a light source, followed by a copper sulfate filter (to remove heat radiation) and an ultraviolet filter (to absorb visible light), together with an ordinary glass lens, which was used to concentrate the radiation upon the condenser lens of the microscope, which permitted use of an ordinary microscope for this purpose. For fibers which were properly sized, the Lubex-rosin sizing appeared to adhere as very fine dots upon the surface of the fiber rather than as a film which might serve to block off the capillaries in the fiber. With fibers which were improperly sized, the fiber is partly encompassed with a film of oil; or with very coarse emulsions, the sizing appears as particles or little lumps between the fibers.

The determination of the permeability of the sized paper, called the sizing factor, is determined either on the basis of the tendency of ink to blot on the paper or of water to permeate it. Since this investigation was concerned chiefly with wrapping papers, the permeability to water was of the most importance. Two tests were used to measure this permeability: the thiocyanate test and the roll-up test. In the former, a little box is folded from the paper specimen, which is then placed upon an ammonium thiocyanate solution and moistened inside with a little ferric chloride solution. The time which elapses until the appearance of a distinctly red color is taken as a measure of the sizing. A satisfactorily sized paper requires 60 seconds. In the latter test, a small piece of paper is placed upon the surface of water, after which it first starts to roll up and then begins to unroll because of expansion of various layers in the paper resulting from permeation by water. The time which elapses from the instant the paper is placed upon the water until it begins to unroll is a measure of the sizing. The roll-up test is used for time intervals up to 10 seconds and the thiocyanate test for longer intervals than this. From these tests and data in the literature, it appeared that the time of penetration is inversely proportional to the square of the weight of a square meter of the paper. The measured periods of time were corrected to correspond with a standard weight of 100 g. per square meter by dividing by the square of the weight of the paper and multiplying by 10,000. As a norm for a satisfactorily sized paper, a penetration time of 60 seconds in a paper of 100 g. per square meter was decided upon. For comparison of the results of the sizing tests in graphs and otherwise, it was found convenient to introduce a sizing factor, by which is meant the measured sizing strength (time of penetration) divided by the content of sizing in the paper. This factor really represents the time of penetration which one would find at a sizing content of 1 per cent. In the experiments with bleached sulfite cellulose, the sizing varied in proportion

to the sizing content so that the sizing factor determined for it had significance. However, with kraft cellulose, the factor at the lowest contents proved to be higher than with higher contents of sizing material. Experimental data are presented graphically.

Analytical procedures were developed to determine the rosin and oil content of sized paper. For rosin sizing only, the paper was extracted with alcohol; the extract was evaporated; and the residue was weighed after drying for a short time at 110 C. For Lubex-rosin sizing the paper was extracted with 1:1 benzene-alcohol mixture. The extract was evaporated, dried, and weighed to determine the total sizing content. The Lubex-to-rosin ratio was determined as follows:

Dissolve the extraction residue in alcohol-benzene (40:60) and add alkali blue indicator. Titrate with NaOH or HCl as required until neutral to alkali blue. This titration indicates an eventual deficiency or excess of alkali in the sizing. Afterward titrate potentiometrically to a point of sudden change at about pH = 7. This titration gives the amount of rosin in the mixture.

One should carry out the titration with an antimony or glass electrode and a sensitive pH meter (vacuum-tube type voltmeter). For the determination of the sizing content of the emulsions, a measured or weighed quantity thereof is evaporated and the residue weighed. The residue can be examined as was indicated above in order to determine its rosin content.

The experimental results of these investigations are presented graphically in the five figures attached to the end of the report, which have been referred to at appropriate points in the preceding discussion.

Three photographs of paper specimens: 1. unsized, 2. sized with Lubex and 3. sized with rosin, on each of which ink lines have been drawn, are attached at the end of the report. On 1. the ink has made a rather blotted and mottled line, whereas with 2. and 3. the lines are clear and distinct, indicating satisfactory sizing for writing paper in these latter two cases.