IPPTA

Silver Jubilee International Seminar & Workshop
Appropriate Technologies For Pulp & Paper Manufacture
In Developing Countries.

New Delhi - 1989

THE SIZING OF PAPER

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Abstract

The paper is mainly dealing, besides a short survey about the development of rosin sizing and its raw materials, with rosin sizing in the neutral area (pH 7), which becomes more and more important due to increasing amounts of calcium carbonate in waste paper.

Up to now the problem of rosin sizing in the neutral area has been the sudden destruction of the sizing when exceeding a certain pH-vàlue. A new product is being presented, that enables a gradually sizing at pH 7 +/- 0,5, as it is not possible with synthetic sizes.

The information will be completed by exact dosing instructions as well as production results of different paper machines.

1. Introduction

When paper is produced nowadays, the optimal and economic sizing receives more relative importance. During the past years the company COLLOD IN CHEMIE from Germany dedicated itself successfully to the overcoming of the chemical problems of paper sizing with its research and development.

As you know, there are two methods to size paper or to give a better term-water finishing, i.e. to control the water uptake of the sheet.

As a method surface sizing is the older one, because until the introduction of rosin sizing the sheets of paper were impregnated with bone glue on the surface. In 1806 Moritz Illig invented not too far from the head quarters of the COLLODIN company in Erbach (Odenwald) the internal sizing with pine rosin; which is today - after 182 years - the most common method to size paper.

In competition to this type of sizing one should think about the above mentioned reaction glues like the ketene dimers or ASA.

But with this essay I want to limit myself to rosin sizing while paying special attention to sizing within the high pH range around 7.

2. ROSIN

2.1 Rosin types and their production :

As raw material for the production of rosin size one employed three of the following different standard types, that differ in production :

wood rosin
gum rosin
oil rosin

Wood rosin is extracted from stumps of conifers, by processing them to chips after they rottened for a few years and then extract the rosin with toluol or other solvents. This type of rosin has lost its rank for contemporary size production.

Gum rosin is cropped by cutting of conifers - usually species of pine during the growth phase. The tree receives two oblique cuts, so that the outflowing gum drips into a container attached below.

This gum contains besides approximately 80% rosin 20% terpentine, which is removed by steam destillation. According to the desired colour the remaining rosin is treated with chemicals or further refining in Vacuo.

Tall oil rosin is – as it is indicated by name – gained from crude tall oil, which results from pulp production after the Kraft process. Tall oil contains more or less rosin acids depending on the composition of the wood. This oil can be fractionated into three compounds fatty acid, tall oil rosin and pitch. In contrast to gum rosin tall oil rosin contains no more terpentine, since it dissolves during light ends.

2.2 Origin of the rosins

Most important supplier of gum rosin is the People's Republic of China, followed by Portugal, Honduras, Mexico, Brazil, Russia and India.

Tall oil rosin is mainly supplied by Scandinavia and the USA, since it is tightly connected with production of Kraft pulp. In 1987 th FRG imported approx. 68 000 tons of rosin whereby a considerable part passes into printing ink and adhesive production.

2.3 Composition of the rosins

Main component of the rosins used for size production are rosin acids, which are reproduced on the following graphs :

Two standard types can be distinguished : One type derives itself from the structure of the abietic acid and differs only in its isomeres by the position and number of double bonds, whereby the levopimaric and palustrinic acids assume special significance, as shall be demonstrated further below. The other type is the one belonging to the pimaric and isopimaric acids, characterized by two isolated double bonds, one of them is localised outside the ring structure. The percental distribution of the acids differs, depending on the origin of the rosin and the method of its production.

Rosins are usually characterized by colour, acid number, non-detergent fatty matter and ash; in the case of the tall oil rosins by their fatty acid content.

2.4 Modification of the rosins

In order to produce paper size from the above mentioned rosins, you have to "fortify" the raw rosin acid, i. e. you modify the rosin at 180°C to 200°C with approx. 8 -13% maleic acid anhydride or fumaric acid. The reaction mechanism is in accordance with the Diels-Alder-cycloaddition, that you can see outlined below.

First essential for this reaction is a rosin acid with two conjugated double bonds, thus acids of the abietic type, which furthermore must have the cisconfiguration.

Such conditions exist only with the levopimaric and palustrinic acids. In the case of the dehydrated abietic acid such double bonds in cis-position exist, but they are part of an aromatic system and probably do not react under the described reaction conditions. A fourth six-membered ring with only one double bond develops out of the two conjugated double bonds of the rosin acid and the double bond of the maleic acid anhydride and/or fumaric acid. Since the fumaric acid takes more space, higher temperatures become necessary for the reaction, than in the case of the maleic acid anhydride.

The meaning of this reaction - unscientifically labelled as "fortifying" - is the introduction of two additional carboxyl groups, which increase the sizing properties of the rosin acid molecules. The modified rosin is often characterized by indication of the acid number in mg KOH/g rosin. The unmodified rosin has an acid number of approx. 165-170, while rosin reacted with 10% maleic acid anhydride shows an acid number of approx. 210.

The stability of the anhydride-ring is of interest for the chemist, since it is still detectable by infrared spectroscope in fully saponified sizes.

If one uses maleic acid anhydride or fumaric acid as dienophile depends on the conditions of operatioin, sizes fortified with fumaric acid usually tend to less foaming.

In conclusion it shoud be mentioned, that up to this day no scientific explanation for this conversion reactin exists. Here one could find excellent opportunities for research.

3. ROSIN SIZES

3.1 Rosin size types

The rosins processed by the Diels-Alder method are usually saponified or dispersed in water.

For production of soap sizes the not yet fortified rosin is saponified with sodium hydroxide or soda (sodium carbonate) and standardized at usually 25% dry content. The special merits of these products are easier handling and storage.

The production of rosin dispersions is a little bit more complex. During stirring the molten rosin is compounded with a protective colloid, usually a hydrous alkaline casein solution, first one produces a water-in-oil emulsion, then changing into an oil-in-water emulsion. The problem is to hit the end point exactly within the temperature control, because otherwise one gets an dispersion too coarse, whose effectiveness is bad and in addition to this tends to depositing. Suitable for raw rosin production one can either employ maleic acid anhydride as well as fumaric acid.

3.2 Application of rosin size

The application of these soap sizes takes place in the conventional manner. One fixes the glue on the cellulose fibre with aluminium sulphate at pH values between 4.5 and 6.8, whereby soap sizes require more acidy conditons than dispersions. Which system is applied, depends finally on the pulp, the mechanical conditions and in paper production as another important factor, how it was always done. Now you may justly ask, why talk about the subject of neutral sizing, if one can already size with rosin sizes at pH 6.8, but unfortunately this applies only for the more or less ideal conditions, mostly for wood-free production. In addition does the effectiveness decrease if one goes beyond a certain pH value limit- in most cases 6.8-, i.e. even a drastic increase of the dosing portion does not show any influence.

4. NEUTRAL SIZING

4.1 Development

Since it is rare to find ideal conditions for paper production, we considered how one could solve the hydrophobic problem near the neutral point with the size.

Not just because we are rosin size producers did we start with the rosin, but because with rosin size you can produce almost any of the current types of paper and cardboard, and in addition to this : with rosin we got a raw material, that cannot be multiplied infinitely.

The problem with conventional rosin sizes is , that with pH value 7 they do not show any further properties, so that even a higher apportioning is not successful.

Aim of our research was to take the rising calcium carbonate and waste paper share into account and to enable a stable operation at pH 7.0 +/--0.2 with minimum amounts of aluminium sulphate. Another ambition was of course to keep the effectiveness in an acidy environment, in order to avoid change-overs for special paper qualities, which would take a lot of effort.

Due to various experiences we have chosen a rosin dispersion, since a number of customers implement already an almost neutral type of sizing, despite the fact that in the meantime first experiences with soap sizes exist.

The raw rosins were subject of another modification and also the protective colloid system was adjusted to the retention in the neutral range.

What I just pointed out with a few sentences, took almost five years until we dared to take the step from the paper lab to the machine, which functions troublefree since then. Without the support of our partners outside this research would have been virtually impossible.

4.2 Application

The most time consuming problem is the application technology realization in the factory, since each production has its individual existence, when a product is manufactured. Condition for the success of this realization is the staff backing the tests and not to get nervous once the computer results first start to flutter.

Since quite a number of companies belonging to the chemical industry live of the paper industry, it is clear why in most cases a whole range of chemical products is added to the paper.They are to be checked and sometimes objectively put into question in regard to effectiveness within the desired system.

First of all one got to find the optimal dosing spot, which is not always easy, because where one thinks it could work, is already something else proportioned and this spot is vehemently defended; or no nozzle for chemical equipment exists, but usually after some searching a dosing spot is found, that can be changed again once the test proceeds or later on in production.

On this chart I have outlined the constant part of the machine and marked some possibilities for dosing, under any circumstances it should take place continuously.

As dosing spots one could consider the overflow box or the thin-pulp area before the vertical screens. In any case one should go as close as possible to the head box, whereby one has to watch with scrutiny what else is dosed, to prevent unwanted reactions resulting from incompatibilities. It is advantageous to place the aluminium sulphate dosing into the white water or behind the fan pump. Depending on the conditions of operation one can dose also at the same spot. It is merely a question of mixing, i.e. the turbulence.

For fixing of one kg rosin approx. 300 g aluminium sulphate are used.

4.3 Fixing agents

We considered how one could substitute aluminium sulphate in a satisfying manner, since sizing in the waste paper sector is limited by low molecular substances, whose removal with aluminium sulphate does not always succeed.

These considerations led to a fixing agent for the described rosin dispersion, allowing toi do without aluminium sulphate. The function is not just ensured by the very low dosage of about 0.05 - 0.3% commercial substance in relation to production, but rather the costs stay within the scope of aluminium sulphate.

Tests have shown, that the size retention stays at first independent from the amount of fixing agent. We obtained pretty good results with the constant application of 0.1% fixing agent and varied the Cobb value Via the amount of size - as I have sketched for you below.

5. PRODUCTION RESULTS

Now that you know that the system is working you would also like to know for what type of production. On the next chart I compiled the qualities used for production.

This applied for example to paper with 175–400 gsm, as raw material 100% waste paper, Cobb (30) approx. 20–40, size approx. O.5% abs. dry, aluminium sulphate 0.15 and/or fixing agent 0.01% tellquel.

Another operation operates 80–230 g qualities made from 100% waste paper, depending on the quality either unilayered or doublelayered, with a long sieve machine with upper sieve, width approx. 4.3 m at 8 - 14 t/h with approx. 300 m/min. The theoretical Cobb (120) is 35, achievable with 0.2% abs. dry at pH 6.2.

Furthemore a paper mill is employed for production of 70–130 g papers. Rosin size application approx. 0.8% abs. dry, Cobb (60) approx. 20-24, aluminium sulphate approx. 0.25 and pH values from 6.3 to 7.2; relatively lots of calcium carbonate, the measured surface pH values reach up to 8.5.

This system works also with wood free papers and is applied for 70-110 gsm. Rosin application 0.8-1.0 pH" value 6.9 - 7.3 Cobb (60) 15 - 22, size press.

Finally we made first experience with five-layered and seven-layered card-board and good results.

6. SUMMARY

Summing up, we can report, that a purpose-made product for the Indian paper production was developed and applied and tested in tropical countries (South East Asia).

Efficiency and presence on the market, as well as the effective and optimal transformation to the new product Collodin rosin size B 300 is ensured by the construction of a production facility in India, which is supposed to start production in close cooperation with Khaitan International, Calcutta/Delhi in the near future.

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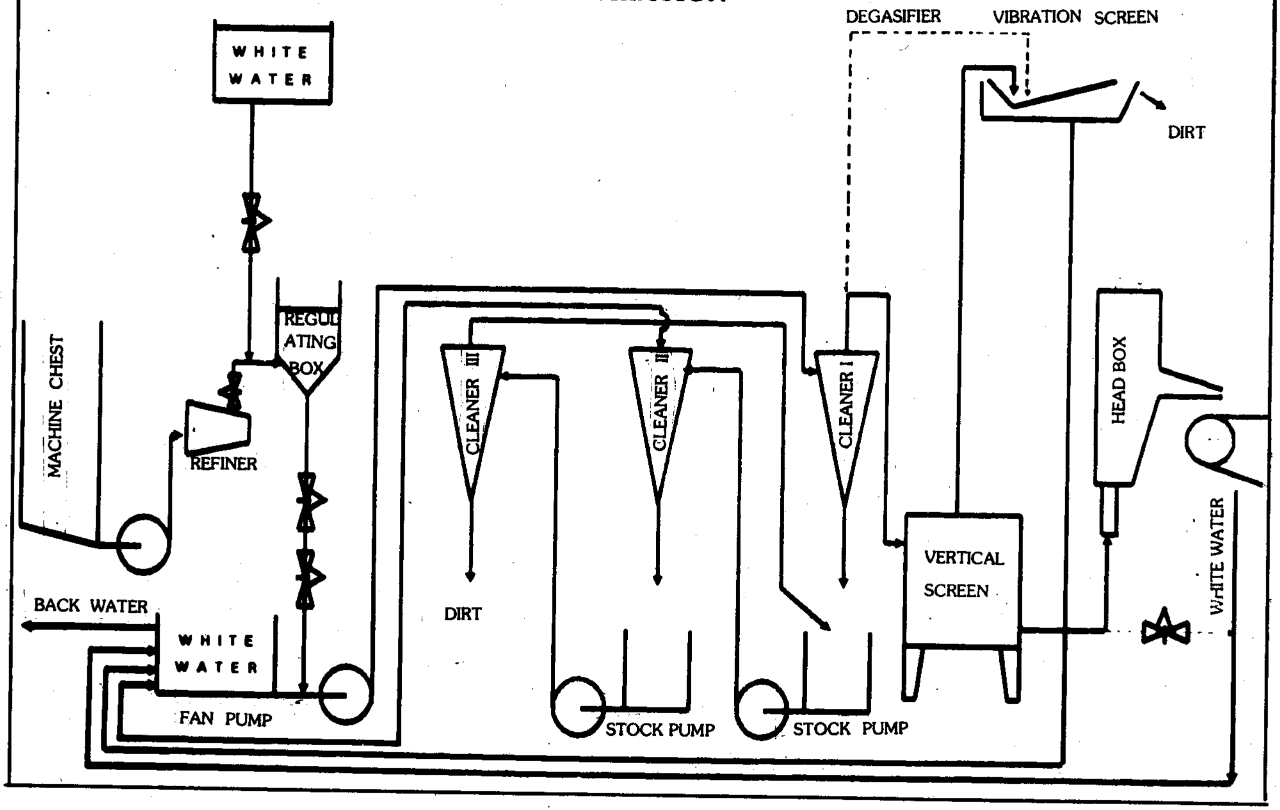
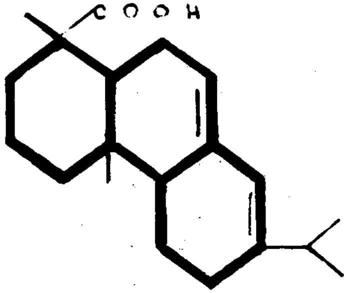
TABLE - III
AVERAGE RESULTS OF PRODUCTION

P M	Raw Material	g/m²	Cobb (sec)	P H	% SIZE Bone Dry
FOUR-DRINIER	100 % WASTE	175/400	20/40(30)	6.8±0.2	0.5
FOUR-DRINIER BELOBOND FORMER	100 % WASTE	80/230 1 + 2 LAYERS	30(60)	6.5±0.3	0.2
FOUR-DRINIER	WASTE/ CELLULOSE	70/130	20/24(60)	6.8±0.5	0.8
FOUR-DRINIER SIZEPRESS	CELLULOSE	70/110	15/22(60)	7.1±0.2	0.8–1.0
CYLINDER	100 % WASTE	500 5 LAYERS	50(60)	7.0±0.2	1.0

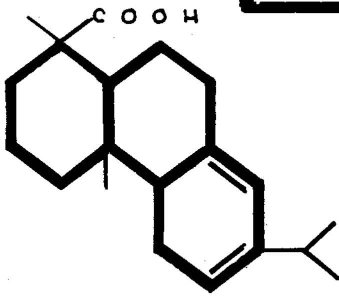
STOCK PREPARATION



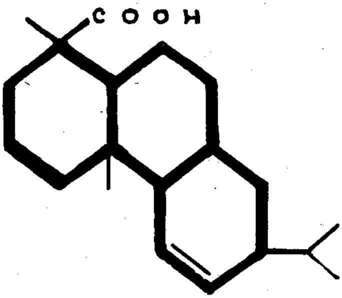
ROSIN ACIDS



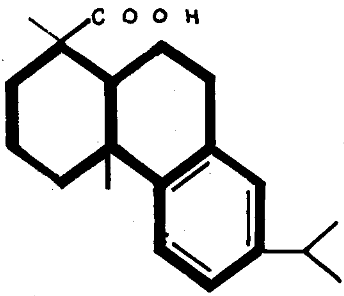
ABIETIC ACID



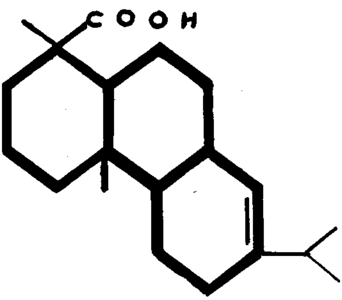
LEVOPIMARIC ACID



PALUSTRIC ACID



DEHYDROABIETIC ACID



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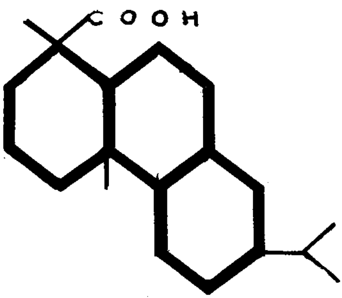
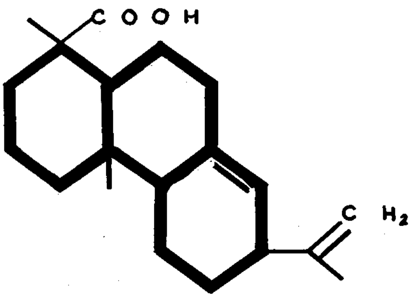


TETRAHYDRABIETIC ACID

ROSIN ACIDS



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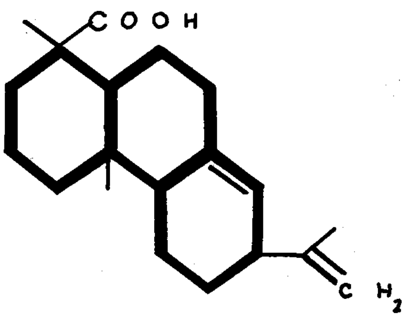
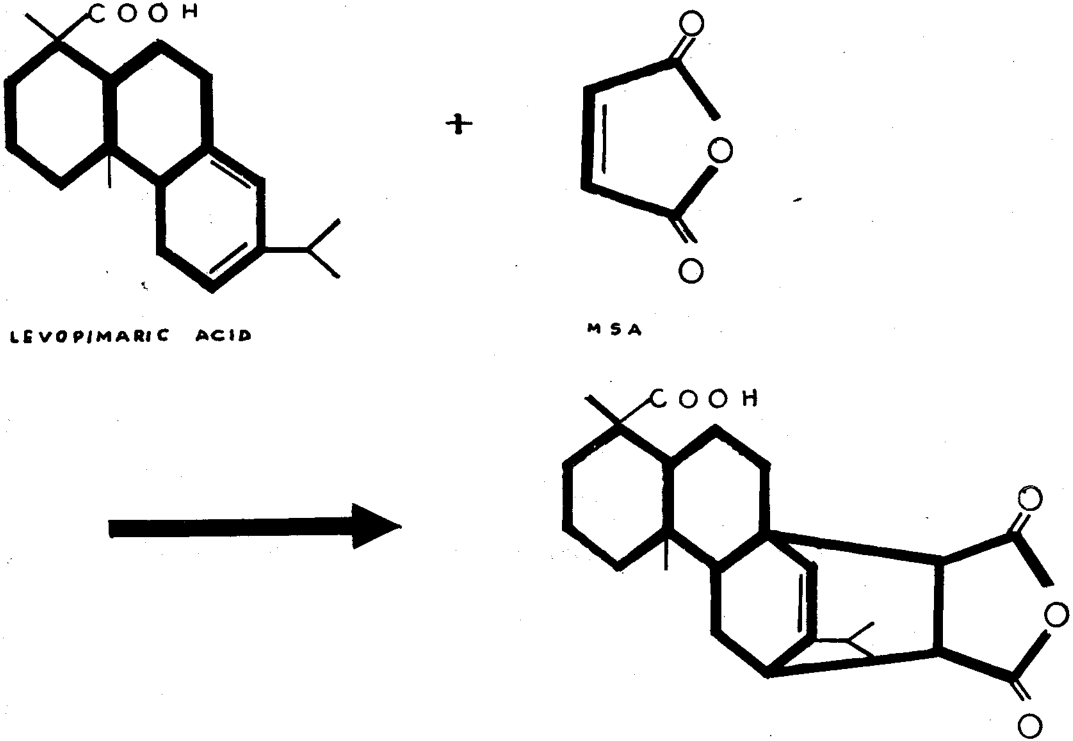


ISOPIMARIC ACID

COLLODIN CHEMIE

DIELS – ALDER – ADDITION



COLLODIN CHEMIE

RELATION BETWEEN
COBB-VALUE AND
ADDITION OF SIZE