Recent developments in neutral and alkaline sizing in Europe

Dr. LONGIN PLACZEK*

In the past ten years we were facing a rapid change in paper making technology in Europe in so far as clay as a filler and as a coating pigment was partly or fully replaced by calcium carbonate.

This fact influences the total paper industry in Central Europe where roughly 40% of paper is recycled.

So papermaker looked for an economic size-system that could be used generally in the presence of Calcium-carbonate The size producers took up this challenge and introduced new neutral sizing systems.

Last, but not least we found that older books and documents printed on acid sized papers show upcoming aging defects, i.e. yellowing of the paper and brittleness. Therefore the new standards for cultural paper products demand or will demand, if not published yet, paper properties like a pH-reaction up to 8.5 and the content of at least 2% Calcium carbonate.

1. The Tradition and the market demand in sizing

In Europe traditionally there are a series of products available that were utilized for sizing purpose in the paper industry. These products can be diversified into two groups, i e soaps and emulsions (Fig-1).

Soaps and conventional emulsions of this kind need dissolved aluminium.sulfate (the papermaker's alum) for the so-called acid sizing (Fig.-2).

About 1960 they introduced the netural sizing by means of "Aquapel" a cellulose-reactive size. This size was introduced in few paper mills producing high grade fine papers with a constant and uniform production program. Another step was made into the paperboard production for milk cartons.

As is the term neutral sizing, actually European paper mills used to apply "Aquapel" in the pH-range 6.5-7 when starting. Later the pH-range changed to the alkaline side pH 7-8.5.

Fig-1

SOAPS	EMULSIONS
ALL ANIONIC (NEGATIVELY CHARGED)	
ROSIN ACIDS	ROSIN
FATTY ACIDS	WAX AND PARAFFIN
FORTIFIED ROSIN ACIDS	FORTIFIED ROSIN
	BITUMEN
	TALLOIL

CONVENTIONAL SIZES WERE ANIONIC SOAPS AND EMULSIONS. FROM THE 50IES TO THE 80IES THE FORTIFIED (MODIFIED) ROSIN DOMINATED BY AND BY THE MARKET IN EUROPE.

*Simonskall 49
D 5165 Hurtgenwald
Germany.

FIG-2

PRODUCT:	SOAP		EMULSION	
Raw Material Base:	Rosin	Fortified R.	Rosin	Fortified R.
pH Range in stock	4–5.0	4.5-5.0	4.5-5.5	5.5-6.5 (7.0)
Continuous Dosage:	RECOMMENDED		RECOMMENDED	
Dilution % S.C.	5	5	5 Less	5 Less
Precipitation	————Alum————			Alum +(PAC) Aluminate
Calciumcarbonate	————Not Applicable————			Applicable in near neutral size system
Talcum	————Applicable————			Reduces pitch trouble
Vegetable Gums	————Applicable————		Better dry + Wet strength retention	

The application of emulsions replacing soaps reduce the dcmand of size and alum considerably. Fortified rosins are even more effective.

FIG-3

CATIONIC EMULSIONS
(Positively Charged)

Cellulose Reactive	Synthetic Polymer	Invrted Emulsion
Alkylene Ketene Dimer (AKD)	Polyacrylates	Fortified Rosin
Alkylene Succinicanhydride (ASA)	Polyurethans	

The new generation of size is cationic based. AKD was first introduced for internal paper sizing in Europe. For special application polyacrylates and ASA were following. The inverted emulsions based on fortified rosin took over the dominating part in sizing finally in Central Europe.

Since the cellulose reactive size, a cationic emulsion, has to be dosed continuously and severel precautions have to be made, the circle of users remained limited. In the same period the fortified rosin was introduced in European mills.

A large potential market opened by the time when nearly the time total paper industry had to change to neutral sizing. This is the field of the new cationic "inverted emulsions", the utilization of which we shall discuss later (Fig-3).

2. Diversitifications in Neutral and Alkaline Sizing

The classical neutral and alkaline size is represented by the alkylene ketene dimers (AKD) introduced to paper sizing and patented by Hercules Corp. (USA). Among a series of other products AKD is followed now by a second product the alkylene succinic andrydride (ASA). The use of the latter product is up to now limited, primarily applied in bleached board and gypsum paper board. The reason might be the shorter shelf life of the emulsion. Therefore the mills have to emulsify ASA in their own plant. The main difference between AKD and ASA is the curing temperature and curing speed.

AKD and ASA belong to the cellulose reactive sizes. They form a covalent bond with the cellulose which is extremely resistant to hydrolysis. This fact often gives problems in recylling of waste paper and mill cutting. But there are benefits which might be named

- improved strength properties of paper
- utilization of $CaCO_3$ as a filler
- reduced effluent loadings
- high sizing degree

The application of neutral sizing in large scale started in the 80ies after a previous period of development in laboratories. The application range, you can compare in Fig-4.

FIG-4

Product:	Cationic Inverted Emulsion	Cationic	Emulsion of
Raw material base :	Fortified Rosin	AKD	ASA
pH-Range in stock	6-7.5		6.5-8
Continuous Dosage	Recommended		Demanded
Dilution % S.C.	5		Less 5
Fixing Agent :	Alum. PAC		Cationic Polymer
	Cat. Polymer		No Aluminumions
Calciumcarbonate:	Applicable		Applicable
Talcum	Applicable		Applicable
Vegetable Gums:	Improved Dry and Wet Strength Retention aid esp. with calciumcarb.		

The demand of Inverted Emulsions is higher but costs are lowercompared to AKD or ASA. For fixing with Inverted Emulsions 0.1-0.5% alum or PAC (Polyaluminumchloride) are used. In the same range, you use cationic polymers, for fixing and pre-coagulation of trash with all systems respectively.

Mainly technical reasons are regarded to be responsible for the rapid introduction of the new cationic modified rosin emulsions. The basis of this size are fortified rosins in a special emulsion system (Inverted emulsion).

They are used with calciumcarbonate fillers. They are working with cellulose fibres, with incrusted fibres and with ground wood in the pH-range of 6.0-7.5. Lignin and dissolved organic materials (trash) do not disturb the size either, if properly applied.

Besides, there is another important advantage with the inverted emulsions, the size degree can be tested immediately after the paper leaves the machine and it is easy to get any degree of sizing (low or higher cobb value) with the new emulsions.

For smaller paper mills producing different paper qualities, it is still of importance that Aluminumions do not disturb sizing. Most benefits in a neutral alkaline system are based on the higher pH-range in the stock as shown in the following figures.

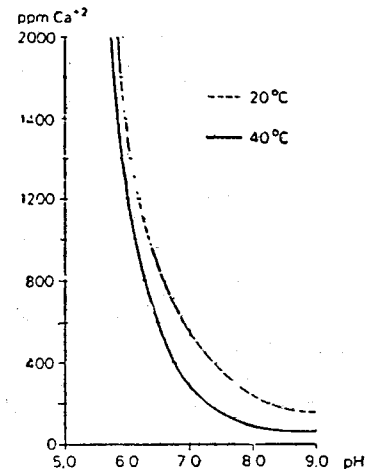
FIG-5

NEUTRAL PAPERMAKING TODAY

BENEFITS:

- **Reduced Chemicals in closed systems**
- **Less Corrosion**
- **Faster Refining at higher pH**
- **Higher strength properties**
- **Less foam**
- **Better retention control**
- **Less backwater solids**
- **Less deposits**
- **Reduced calciumcarbonate dissociation**
- **Neutral product**

FIG – 6



SOLUBILITY OF $CaCO_3$ DEPENDING ON TEMPERATURE AND pH
FREE Ca : IONS DISTURB SIZING

3. The Utilization of the new inverted emulsions

Nevertheless there remain problems in sizing with inverted emulsions too.

- Sizing takes place in the temperature range up to 60°C only. Many European paper mills apply elevated temperature in the headbox for a better drainage on the wire.
- Silicates and phosphates in the stock distrub or even hinder the sizing These substances often comes into the stock from the recycling procedure, the deinking process.

Sizing with inverted emulsions should be carried out continuously. This means you first add the fixing agent at the fan pump for better distribution. Not far from the headbox you use the turbulance for instance in the overflow of the levelbox for adding the dilute emulsions. Addition of alum or PAC afte dosing of the dilute emulsion is practicised too due to results obtained.

4. Sizing calciumcarbonate loaded papers

When changing formulation of the paper stock replacing clay with calciumcarbonate the cobb value will go up. This means the size degree will be reduced.

Collodin company experienced that the average cobb value of 25 achieved with a clay filler will change to 35 when replacing it by calciumcarbonate.

FIG.—7

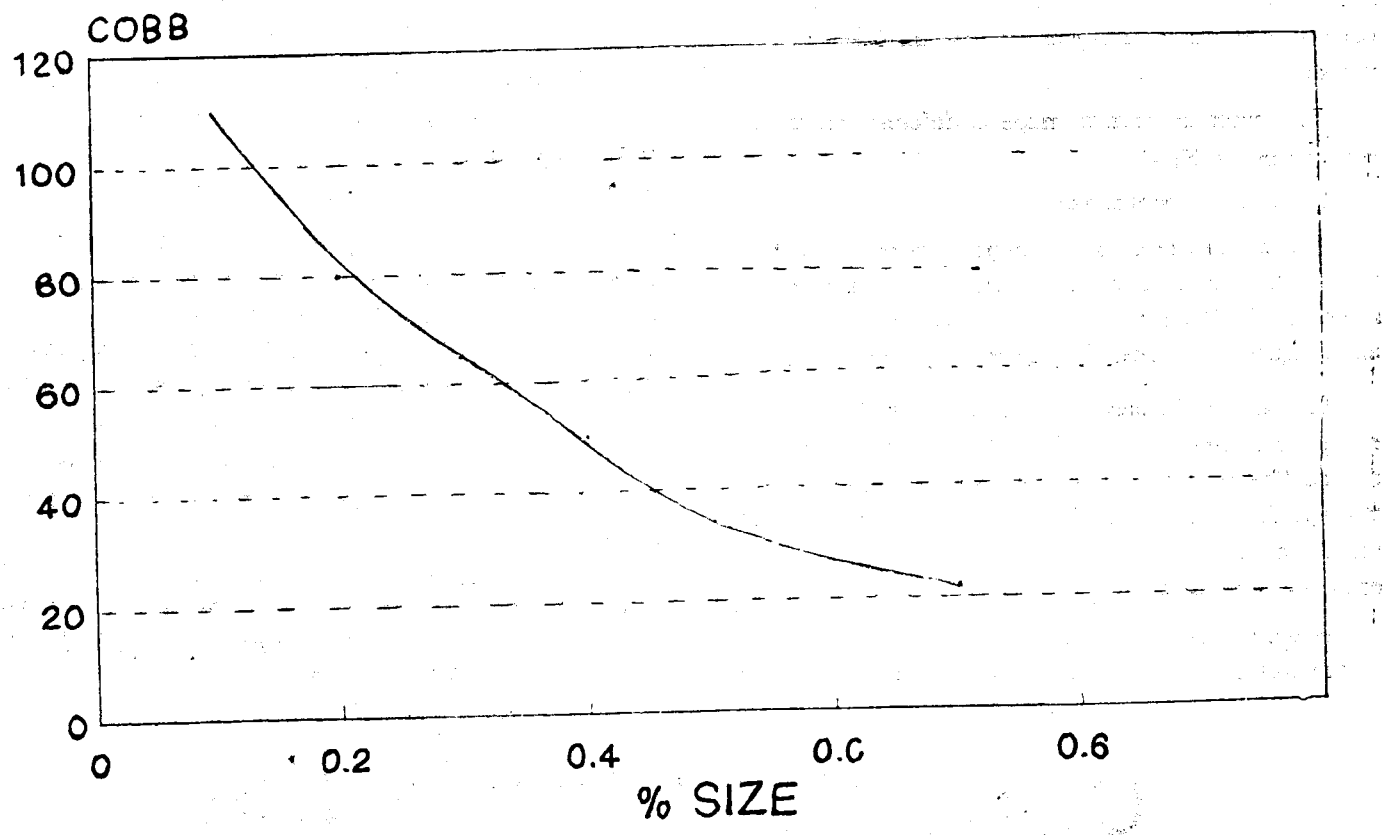


FIG —8

AVERAGE RESULTS OF PRODUCTION

P M	RAWMATERIAL	g/m²	Cobb (see)	pH	% SIZE BONEDRY
FOURDRINIER	100 % WASTE	175/400	20/40 (30)	0.0±0.2	0.5
FOURDRINIER BELBOND FORMER	100 % WASTE	30/230 1+2 LAYERS	< 30 (60)	0.5±0.3	0.2
FOURDRINIER	WASTE/CELLULOSE	70/130	20/24 (60)	0.8±0.5	0.8
FOURDRINIER	CELLUOSE	70/110	15/22 (60)	7.1±0.2	0.8-1.0
SIZEPRESS CYLINDER	100% WASTE	500 5 LAYERS	50 (60)	7.0+0.2	1.0

In any case the use of calcium carbonate implicates a higher size consumption due to the fact that calcium-loaded papers have a higher volume and an elevated porosity.

Few practical results made in different paper mills can be seen in Fig-8.

5. Review and Conclusions

Historically seen the European paper mills made their own sizes or decided the way of development for a period of 150 years. In the past 40 years the chemical industry introduced new developped products.

In Europe the classic rosin soaps have been replaced by emulsions (also called dispersions) to a large extent. The raw materials basis changed from natural rosin to fortified rosin. Based on fortified rosin the anionic emulsions lost ground in the favour of cationic emulsions in the past 5 years.

A special development took place in synthetic sizes in the past 30 years. These products based on cellulose reactive substances as AKD and ASA are said to win a considerable but limited growth in the production of fine papers and specialty paper board.

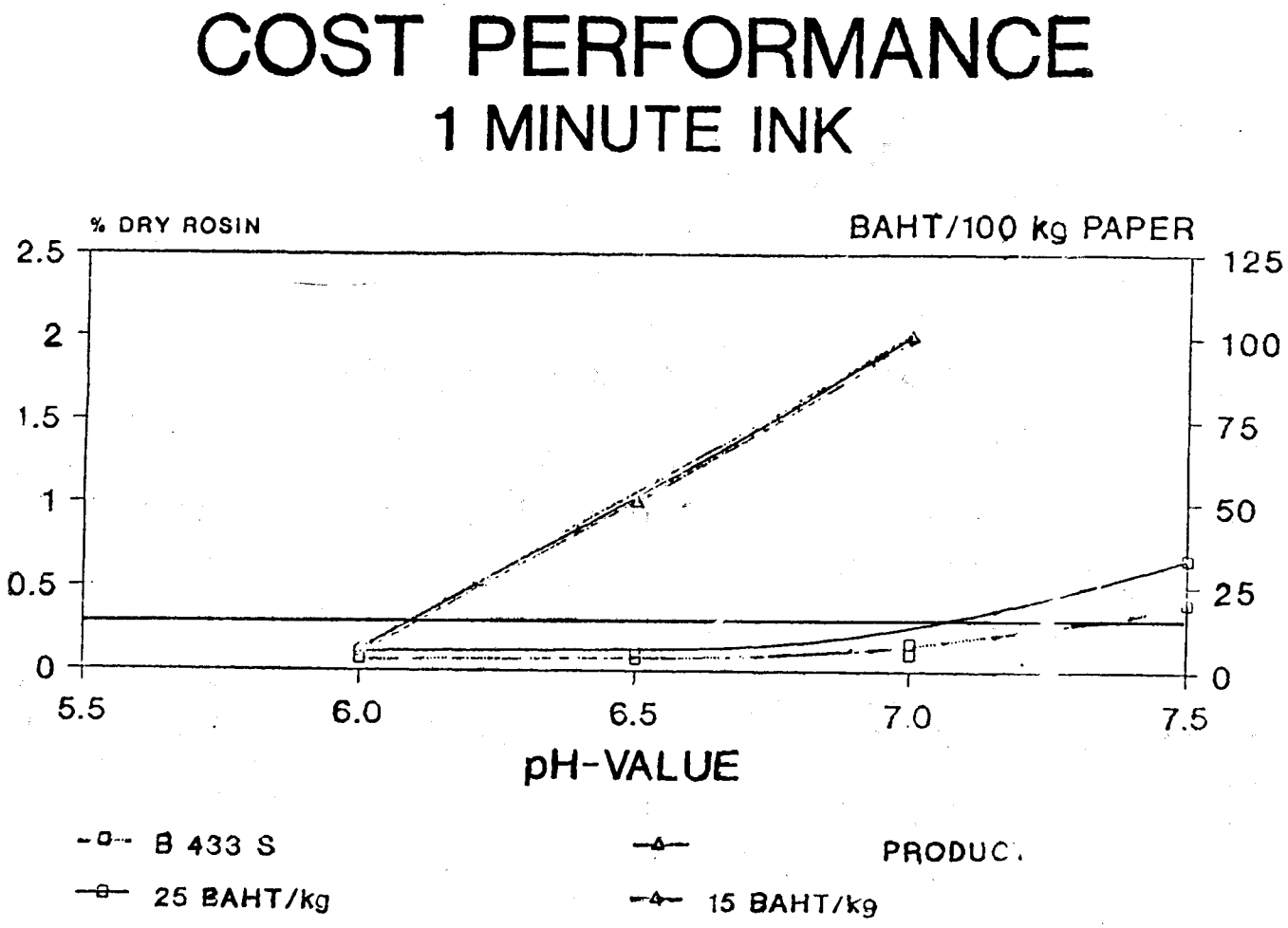
The new generation of sizes is cationic based.

It is a common experience that the European technology cannot be transferred to India or Asia without a proper adaption.

The raw materials in the paper stock are different. Over there wood pulps here non-wood pulps. The quality of calciumcarbonate (mainly ground lime-stone) is higher in Europe and the costs are lower there. Comparison are made with localy available qualities and PCC (precipitated calciumcarbonate).

Sizing in the quasi neutral range above pH 6.7 to 7.5 is efficient and economic with "Inverted Rosin Emulsions" (Fig-9). For fine papers based on cellulose fibres and loaded with calciumcarbonate for neutral or alkalin sizing the cellulose reactive sizes can be utilized in order to achieve high brightness, opacity, bulk and last not least a high sizing degree.

FIG.—9



TABLE—1

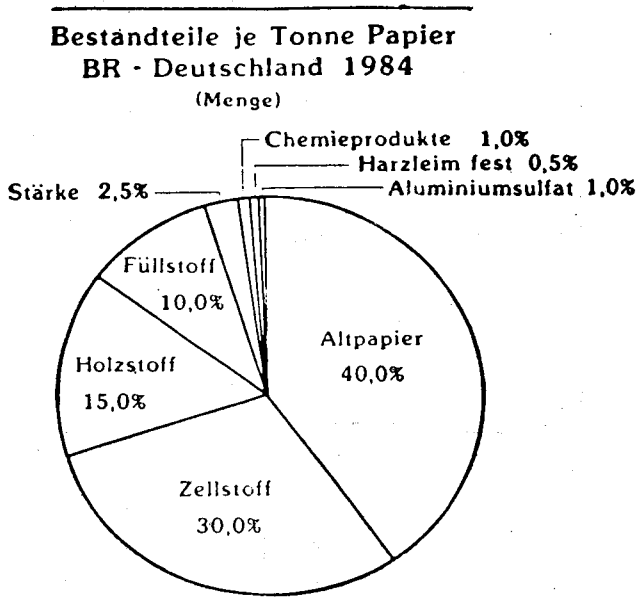
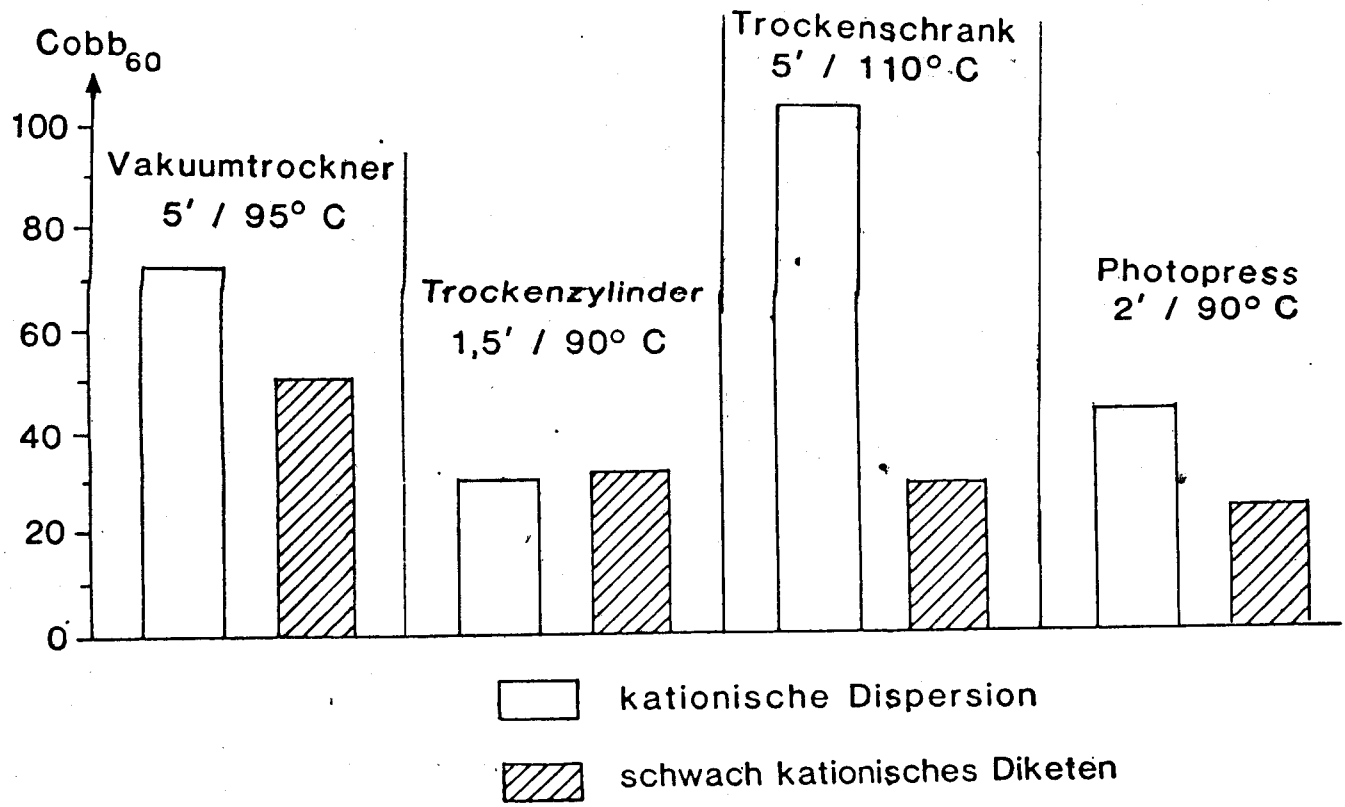


TABLE -2

Leimungsmittel		Schutzkolloid		Beispiele	Anwendungs-bereich	
Ionogenität	Polymerisat	Ionogenität	Polymerisat		Masse	Ober-fläche
kationisch	ja	—	—	Acrylester-Dispersionen, Polyurethane	+ +	+ +
nichtionisch	nein	schwach kationisch	ja	Fettalkyldiketen, Subst. Anhydride	+ +	(+) —
nichtionisch	nein	stark kationisch	ja	Fettalkyldiketen	+	(+)
anionisch	ja	—	—	Styrol-Maleinat-Copolymere	—	+
nichtionisch	ja	schwach anionisch	ja	Styrol-Acrylester-Dispersionen	—	+

TABLE-3



REFERENCES :

1. Table 1—3 By Courtesy of BASF (Germany)
2. Fig. 7—9 By Courtesy of Collodin Chemie (Germany)
3. DUMAS D.H , An Overview of Cellulose reactive sizes TAPPI 1981/1 P—43/45
4. WEIGL., J. Papierherstellung im Schwach Sauren und Alkalischem PH, Wochenblatt fur papierfabrikation. 1982/23-27, P. 857
5. SCHULTZ DR,, Modern Paper Sizing Lecture held October 14, 1989 in Bangkok