Industrial gypsum as a coating pigment

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Hydrated gypsum grades of different origins are suitable for paper coating provided pigment and color systems exhibit a high level of mechanical and chemical stability and, particularly, if pigment blends are used in the color formulations.

Over the past few years, worldwide consumption of graphics papers has risen continuously. In 1988, global production figures reached 20 million metric tons of coated paper and 12 million metric tons of coated board (*1*).

In Europe, the Federal Republic of Germany dominates the coated paper sector, accounting for approximately 30% of total production and 26% of consumption (*2*). Base materials account for about 70% of overall costs, another 13% is spent generating energy, and labor, maintenance, and capital costs account for just 17% (**Table I**).

Since coating accounts for about one third of the manufacturing cost of ready-made lightweight coated paper, we must pay attention to suitably modified coating formulations in terms of pigment and of binder compositions—the two most expensive components of coatings.

Coating pigment market trends

The trend toward coated papers is clearly reflected in the latest figures on coating pigment consumption (**Fig. 1**). By comparison, total consumption of coating kaolin in 1968 was 563,000 metric tons in Western Europe while that of fine-ground natural calcium carbonate was as low as about 13,000 metric tons (*3*).

Some 20 years ago, kaolin was still the dominant coating pigment for the paper industry. The situation is drastically different today. In Western Europe, natural calcium carbonate is a serious competitor of kaolin because of its application benefits and low cost. The kaolin currently used in Western Europe originates from England (68%), the United States (14%), and Brazil (8%) (*3*). The Federal Republic of Germany, France, and Czechoslovakia together share about 10% of the market.

Figures show that the paper industry is becoming a leading consumer of pigments. It takes great interest in the development of new pigment deposits. Factors affecting purchasing decisions are price, availability, uniform pigment qualities, and application benefits.

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I. Exemplary cost structure for the manufacturing of a 50-g/m² (34 lb) LWC grade (coat weight 18 g/m²)

Type of cost	*Share, %*
Raw materials and auxiliaries	70
Manufacturing wages	5
Energy	13
Maintenance	4
Capital	8
Total	100
Coating cost, DEM	0.02

Assumed production: 2.4×10^9 m²/year.

Gypsum and anhydrite from industrial processes

Industrial gypsum and crystal water-free anhydrite are obtained in large quantities as by-products of the industrial manufacture of wet phosphorous acid, hydrofluoric acid, and citric and other organic acids, as well as in the context of ecological measures such as flue-gas desulfurizing and effluent treatment (**Table II**).

Unfortunately, only a minor part of these by-products can be used economically because of process engineering problems (*4*). For the most part, the waste products are deposited in landfills or discharged into the seas. In view of the environmental impact of these methods, it seems all the more desirable to provide for their effective use.

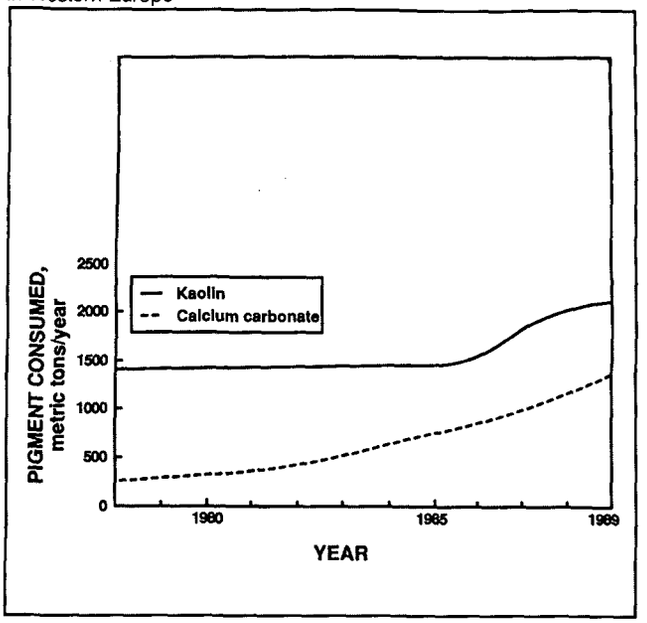
Gypsum modifications and their physicochemical properties

The gypsum system as such has been the subject of frequent studies. Its physical and chemical properties are measured and interpreted in a highly contradictory manner in the pertinent literature (**Table III**).

There are five different types of calcium sulfate modification: dihydrate ($CaSO_4 \cdot 2H_2O$), hemihydrate ($CaSO_4 \cdot 0.5H_2O$), anhydrite III ($CaSO_4$), anhydrite II ($CaSO_4$), and anhydrite I ($CaSO_4$). The hemihydrate and anhydrite III are found as α and β variants, differing only in their crystal structure and in their energetic and application behavior (*5*).

Gypsum is characterized by a high solubility level, which

1. Consumption of kaolin and calcium carbonate as coating pigments in Western Europe



II. Quantities of gypsum and anhydrite worldwide and in the Federal Republic of Germany

Source	*World (1984), metric tons/year*	*Federal Republic of Germany, metric tons/year*
Phosphorous acid production	130 (only 4% reused)	0.8
Desulfurizing plants (flue gas gypsum)[a]	2.5 in Japan	5.0
Hydrofluoric acid production	3	0.26
Organic acid production (citric, oxalic, and tartaric acid)	...	0.80
Natural gypsum	75	3.0[b]

[a] In the United States, desulfurizing processes are converted to flue-gas gypsum.

[b] Approximately.

III. Gypsum modifications and their physicochemical properties

Phase (formula, designation, lattice structure)	*Further designations*	*Crystal water content, %*	*Density, g/cm³*	*Mol. mass, g/mol*	*Water solubility at 20°C, g/ 100 g solution*	*Formation temp. in industry, °C*
$CaSO_4 \cdot 2H_2O$ Calcium sulfate dihydrate Monoclinic	Gypsum, gypseous stone, gypsum rock, industrial gypsum, hard gypsum	20.92	2.31	172.17	0.21	<40
$CaSO_4 \cdot 1/2\ H_2O$ β-calcium sulfate hemihydrate Rhombohedral	β-hemihydrite, β-gypsum plaster of Paris, low-pressure burnt gypsum	6.21	2.619-2.637	145.15	0.88	120-180 (dry)
$CaSO_4 \cdot 1/2\ H_2O$ α-calcium sulfate hemihydrate Rhombohedral	α-hemihydrite, α-gypsum autoclave gypsum	6.21	2.757	145.15	0.67	80-180 (wet)
$CaSO_4$ III	β-anhydrite III	0	2.580	136.14	0.67-0.88	290 (dry)
Anhydrite III, soluble	β-anhydrite III'					290 (dry)
Hexagonal	α-anhydrite III					110 (wet)
$CaSO_4$ II Anhydrite II, insoluble Rhombic	Anhydrite, industrial anhydrite, burnt anhydrite	0	2.93-2.97	136.14	0.27	300-900
$CaSO_4$ I Anhydrite I Cubic	High-temperature anhydrite	0	Not applicable	136.14	...	...

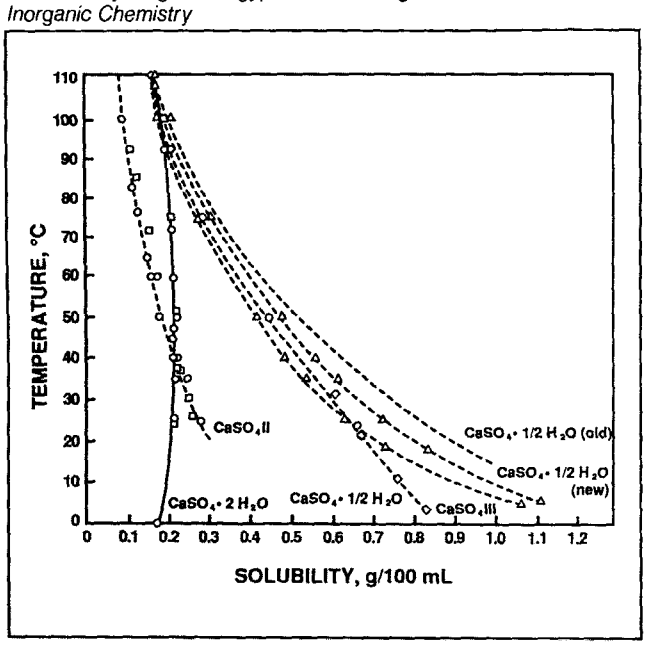
is responsible for poor dispersibility, high dispersing agent consumption, inadequate solids content, and poor compatibility with other coating color components.

For that reason, it is most important to reduce the solution rate of gypsum. However, the characteristic solubility of the individual types of modified gypsum has not been fully clarified. Still open are the questions of potential crystal transformation in water during measuring, dependency of the solution rate (up to 20%) on the grain size (*6*), and the lack of a linear correlation between solubility and temperature (*7*). The solubility values are indicated in **Fig. 2** (*8*).

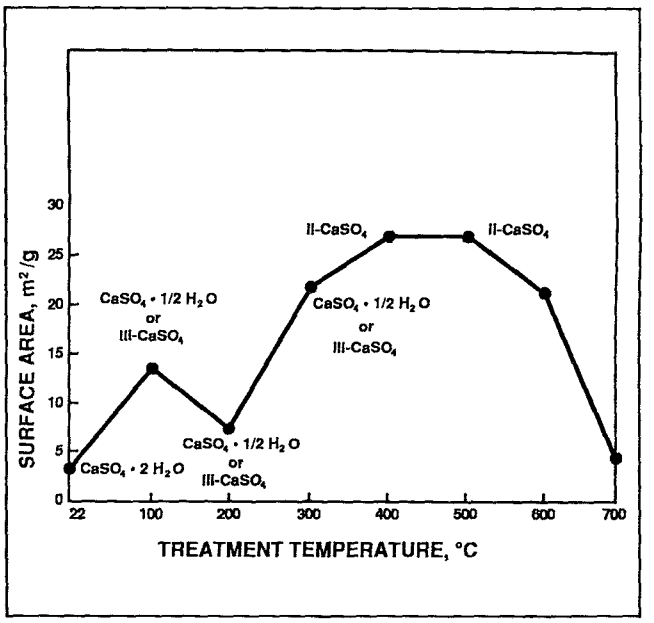
The graphs describing the stable equilibrium of the calcium sulfate dihydrate and of $CaSO_4$ II are shown in solid lines and those for the metastable equilibrium in dashed lines. In accordance with the solubility theory, the "insoluble anhydrite II" is more soluble in its metastable range (below 38°C) than calcium sulfate dihydrate, but far less soluble than the metastable hemihydrate and the so-called soluble anhydrite III.

Figure 3 illustrates the changes in structure and

2. Solubility diagram of gypsum according to *Gmelin's Handbook of Inorganic Chemistry*



3. Crystal structure and specific surface area of heat treated gypsum



IV. Heavy-metal contents of various gypsum samples

Element	*Citric acid gypsum, μ g/g*	*Phosphorus acid gypsum, μ g/g*	*Flue-gas gypsum 1, μ g/g*	*Flue-gas gypsum 2, μ g/g*	*Flue-gas gypsum 3, μ g/g*	*Flue-gas gypsum 4, μ g/g*
Pb	19.0	40.0	14.6	24.2	33.5	33.9
Co	-0.1	15.0	-0.1	-0.1	11.5	15.6
Cr	-0.1	0.85	1.32	1.46	3.27	29.6
Cu	2.0	5.96	1.65	2.72	4.35	7.32
Ni	-0.1	-0.1	0.85	0.38	0.65	1.0
Zn	2.0	1.70	3.85	3.7	3.7	6.32
Mn	87.0	7.95	4.25	186.0	64.0	28.3
Cd	0.01	0.11	0.19	-0.01	0.06	0.01
Tl	1.0	35.2	13.7	3.6	30.7	38.3

specific surface area of gypsum as a function of heat treatment temperature (*8*). Obviously, the specific surface area changes drastically under the influence of heat, which will simultaneously change reactions and overall behavior of these boundary layers.

Use of industrial gypsum as a coating pigment

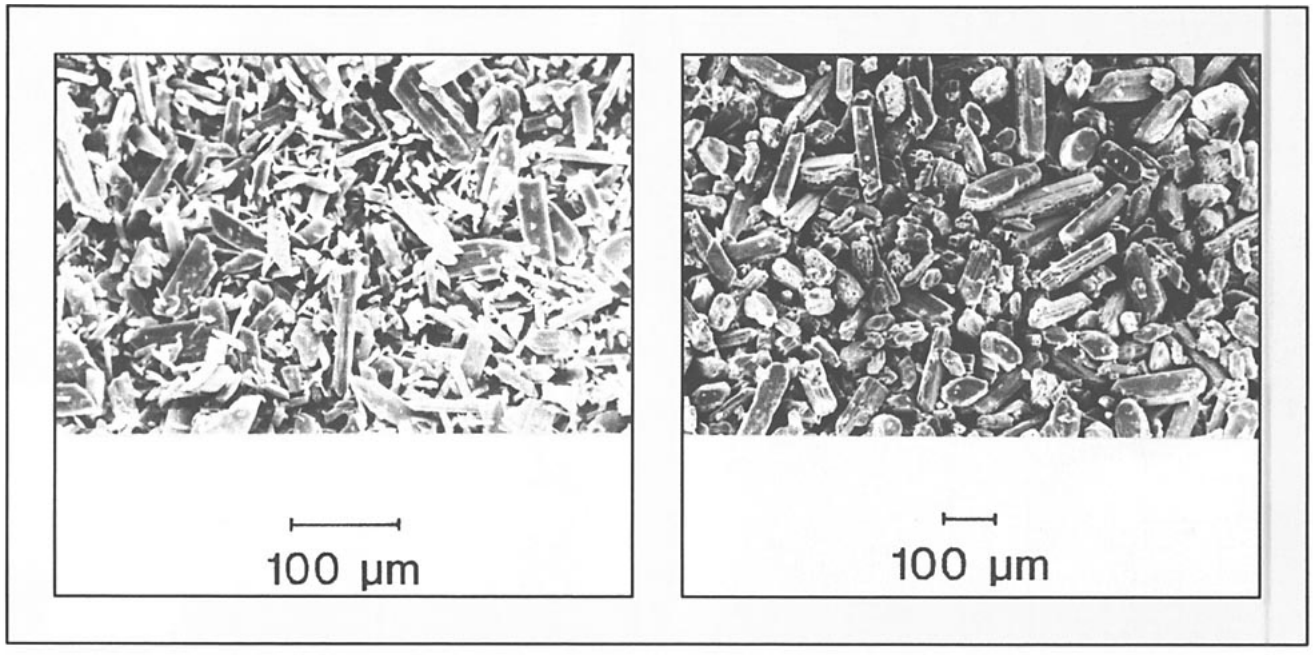
Industrial gypsum has been under discussion in the paper industry since the early '30s as a potential filler pigment. In the '70s, paper coating specialists tried to introduce "Almaline," a precipitated $CaSO_4$, but the attempt failed.

Many publications suggest using the not-very-soluble anhydrite II as a coating pigment (*9*). However, since gypsum is for the most part obtained in the form of dihydrate, expensive recrystallization operations would make the project unprofitable.

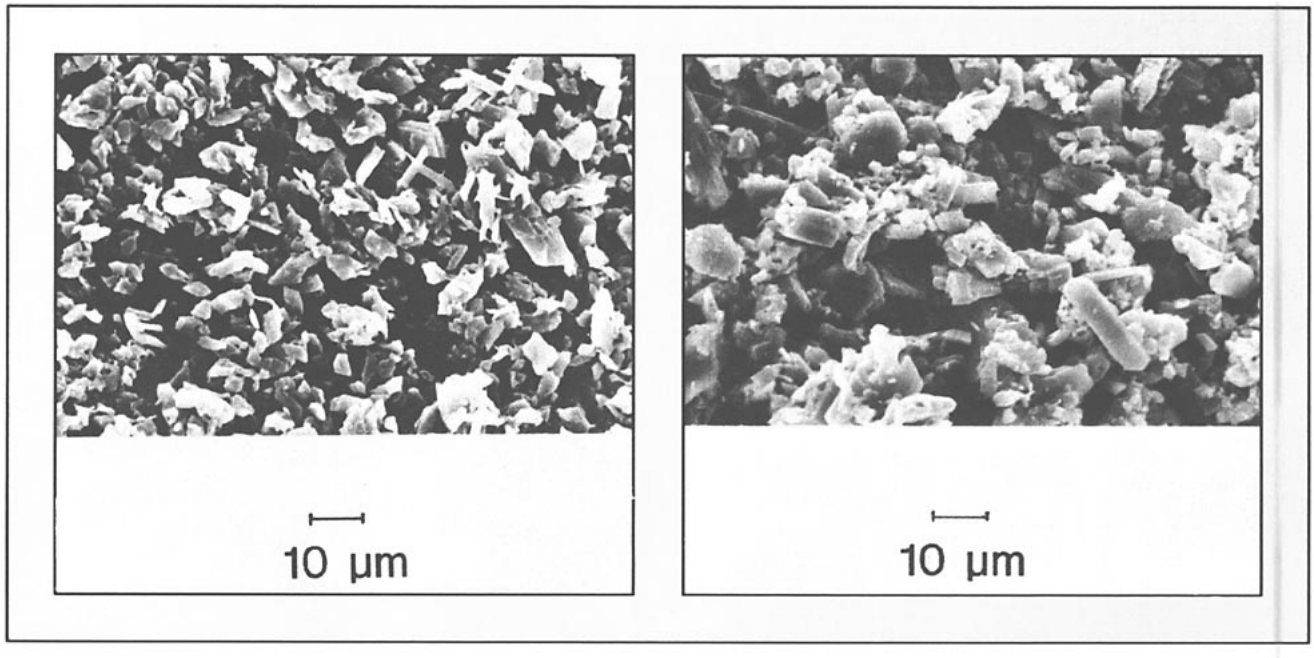
In the form obtained, industrial gypsum is unsuitable for use in the paper industry for the following reasons:

- Excessive contamination levels and low brightness
- Low particle fineness

4. *Unground gypsum. Left: citric acid. Right: flue gas.*



5. Ground gypsum. Left: citric acid. Right: flue gas.



V. Use of market dispersing agents for dispersion of citric-acid gypsum

	Na polyphosphate	*Na polyacrylate*	*Na citrate*
Dispersing agent, %	4.0	1.5	3.0
Solids content, (air-dry) %	57.5	57.5	57.6
Brookfield viscosity			
50 rpm mPa • s	8400	8800	12800
100 rpm mPa • s	4800	5400	6400

VI. Modified polysaccharides used for dispersion of citric-acid gypsum (50% <2 µm)

	CMC low-molecular-weight		*Modified starch low-molecular-weight*	
Dispersing agent,%	2.0		2.0	
Solids, %	57.7	66.6	57.5	67.0
Brookfield viscosity				
50 rpm mPa • s	188	2160	88	1160
100 rpm mPa • s	144	1740	120	860

VII. Viscosity development for gypsum and kaolin blends

Gypsum, %	Kaolin, %	Dispersing agent o.d. related to o.d. pigment (total)	Solids, % (24 h at 40°C)	pH	Brookfield viscosity, 50 rpm	Brookfield viscosity, 100 rpm
80	20	2.0% CMC	66.2	7.6	13,400	8,550
80	20	1.5% polyacrylate	65.6	7.6	7,300	4,400
80	20	2.0% CMC + 1% polyacrylate	66.1	7.4	8,600	5,850
80	20	2.0% modified starch + 1.0% polyacrylate	66.4	7.2	2,800	1,900
15	85	2.0% CMC + 1% polyacrylate	58.6	7.5	32,400	22,200

VIII. Present stage of development of gypsum and kaolin blends

Gypsum, %	Flue-gas gypsum, %	Kaolin, %	Solids, % (24 h at 40°C)	pH	Brookfield viscosity 50 rpm	Brookfield viscosity 100 rpm
50	...	50	66.2	9.9	1520	980
60	...	40	66.3	10.0	1080	680
70	...	30	66.1	10.0	530	345
...	50	50	66.2	9.7	1320	1100
...	60	40	66.1	9.4	700	530
...	80	20	66.9	9.9	530	345

- Lack of water retention
- Excessive solubility
- Poor dispersibility, requiring extensive use of dispersing agents
- Low solids content
- High low-shear viscosity
- Viscosity instability
- Poor compatibility with other coating color components.

As far as good and uniform white pigment qualities are concerned, the industrial gypsum grades available until a few years ago proved inadequate for effective use in this area. With flue-gas gypsum and phosphorous-acid gypsum, for example, heavy-metal ion concentrations were too high and brightness levels too low. The gypsum derived from citric acid production, therefore, showed a pronounced blue tint.

Recently, paper manufacturers have made a concentrated effort to find useful applications for recycled gypsum products.

Physicochemical analyses of various industrial gypsum grades

The heavy-metal contents of various gypsum samples of

IX. Components of the gypsum and kaolin slurry for Field Test 1

Flue-gas gypsum (70% < 2 μm)	80%
Kaolin (75% < 2 μm)	20%
Solids	67.1%
pH	9.2
Brookfield viscosity	
50 rpm	1400 mPa • s
100 rpm	1260 mPa • s

X. Coating color formulation of Field Test 1

Components, %	*Control color*	*Test color*
Flue gas gypsum (70% <2 μm)	...	80
Kaolin (75% <2 μm)	20	20
$CaCO_3$ (90% <2 μm)	80	...
Slip additive	0.8	0.8
Thickener	0.4	0.4
Starch	2.0	...
Synthetic binder	9.5	8.5
Crosslinking agent	0.5	2.0
Optical brightener	0.5	0.5

XI. Coating color test results of Field Test 1

	Control color	*Test color*
Solids, %	64.0	64.7
pH	8.4	8.0
Water retention, s	44	65
Brookfield viscosity, 100 rpm, mPa • s	1600	1080
Haake HSI viscosity	70	26

XII. Paper test and printability results of Field Test 1

	Control paper		*Test paper*	
	Top side	*Wire side*	*Top side*	*Wire side*
Grammage, g/m²	69.8		69.6	
Gloss 75° (Zeiss), %	20.4	18.7	20.8	20.0
Basic whiteness, %	74.8	75.2	71.2	71.4
Xenon whiteness, %	76.1	76.2	73.0	73.1
Opacity, %	92.0		89.3	
Wet pick resistance	OK		Slight ink repellency	
Penetration time, min	10	10	40	40
Wipe test	Slightly micro-porous		Solid	
Field test print	...		Runnability and printability same as control paper	

flue-gas cleaning and citric acid production are listed in **Table IV**. These samples were specifically slated for further industrial use because of their low heavy-metal levels and high brightness levels. Measurements were made using flameless atomic absorption spectrometry methods. Brightness levels (R 457%) of high-purity flue-gas gypsum (no. II) and of separately purified citric-acid gypsum samples ranged from 85% to 91%, AT1000 abrasion from 2 mg to 7 mg, and particle size distribution from 50% to 70% (< 2 μm).

The particle size range of industrial gypsum renders it unsuitable for coating pigment purposes (**Fig. 4**). When the gypsum samples were wet-refined in ball mills, problems were encountered due to their high water solubility and high softness levels. The high solubility requires special refining agent systems, especially if very fine particles are to be achieved. In addition, care must be taken during refining not to destroy the crystal structure (such as platelets or needles) and to prevent temperatures from drifting off, causing a range of uncontrolled reactions due to transformation from dihydrate to anhydrite (**Fig. 5**).

Initial experience gained with gypsum as a coating pigment

The main obstacle to the use of gypsum as a coating pigment is its high solubility, which is responsible for poor dispersibility, high use of dispersing agents, insufficient solids content, and poor compatibility with other coating color components (**Table V**).

Table V shows that the additives commonly used for pigment dispersion are partly or totally ineffective for dispersion of gypsum having a particle fineness of 50% (< 2 μm). The dispersing agent quantities indicated represent an optimum in terms of minimum viscosity. Dispersing agent blends, in turn, yield somewhat more favorable results but only in isolated cases, and the results are still unacceptable.

Coating colors produced at reduced solids content showed unstable viscosities. The processors of these coating colors were faced with the following problems:

- Poor coating color flowback due to excessive low-shear viscosity
- Pronounced strikethrough

- Low paper smoothness levels in spite of high supercalendering pressures
- Very low gloss levels
- Poor coat setting
- Inadequate ink drying
- Low print opacity.

Intensive efforts are being made worldwide to counteract all these well-known deficiencies of gypsum systems. Fundamental research in this area presently focuses on the following objectives:

- Dispersing methods for hydrated gypsum at high solids and low viscosities, which ensure good storage stability of slurries
- Optional blending of gypsum with other pigments, primarily kaolin and calcium carbonate, at any given ratio
- Creating coating colors which, besides standard treatment and processing characteristics, offer high finished qualities for gravure, offset, and letterpress applications
- Avoiding white-water circuit problems due to recycled gypsum-containing coating color and paper broke.

Since there is no satisfactory and profitable solution which eliminates all of these problems, specialists will have to open up new avenues if any advancement is to be realized in this sector.

Development of new dispersing systems on the basis of protective colloids

In the pertinent literature, modified polysaccharides are described to have a dispersing effect on gypsum. Dispersion results obtained are shown in **Table VI**. With up to 67% solids and a dispersing agent addition of 2%, acceptable viscosity levels could be reached via low-molecular-weight modified starch. Similar to other pigments, the dispersing agent requirement of gypsum will increase with particle fineness.

In view of this situation, pigment suppliers have been striving to improve their gypsum products. Today, gypsum slurries of different origins are offered with fineness degrees of 50–80% (< 2 μm) and which exhibit viscosities around 100 mPa·s at 70% solids. For obvious reasons, newly developed refining and dispersing agent systems are being kept secret. It may safely be assumed, however, that these products are combinations of dispersing, complexing, and stabilizing agents.

Coating slurries containing 100% gypsum as pigment can be used directly in the coating color preparation process. However, if gypsum is intended for use on a broader scale, it will have to be blended with other pigments to improve finished paper quality. Blends containing comparatively small proportions of kaolin give rise to serious viscosity problems. This problem area is illustrated by studies of gypsum and kaolin blends, as shown in **Table VII**. If kaolin proportions are increased, viscosities will change as shown in **Table VIII**. If well preserved, these slurries may be readily stored under normal conditions.

Very good dispersion results are also obtained with other dispersing and protective colloid systems based on blends of polyvinyl alcohol, polyvinyl pyrrolidone, and other surface reactant agents.

In this context, gypsum may as well be dispersed cationically.

Coating tests of gypsum-containing coating colors

Initially, tests were conducted with various dispersing systems to try to optimize their solids contents, viscosity constancies, and compatibility with other coating pigments. Afterwards, the dispersing systems were used in trials on a Dixon pilot coater. When gypsum was found to be equally suitable for web offset and rotogravure printing, further coating tests were performed on pilot coaters at elevated coater speeds. The results were very favorable.

These tests showed that if gypsum and kaolin are stable enough to permit storage at low viscosity and in blended form, subsequent color preparation will be more or less free of problems. This is also true if the gypsum-kaolin ratio is altered. However, when this high chemical and mechanical stability cannot be ensured, precipitations may be expected to occur under intensive shear effects such as those found in pressure filters and pumps (*10*).

Coaters having facilities for storing and dosing the two pigments separately usually split up pigments if gypsum is used; they start out with gypsum, to which the remaining coating raw materials and additives are added. Finally, the pigment blend is dosed into the coating color.

In field tests, two alternatives were tried with offset coating colors: direct dosage of gypsum and kaolin blends and split dosage of pigment.

Field Test 1

This field test was based on direct dosage of a gypsum and kaolin blend. A standard color system containing a high percentage of $CaCO_3$ was used as the control sample in terms of processing behavior and end quality.

Table IX lists the data ascertained for a pigment slurry consisting of 80% flue-gas gypsum having a particle fineness of 70% (<2 μm) and 20% English coating kaolin. The compositions of the two coating colors are compared in **Table X**.

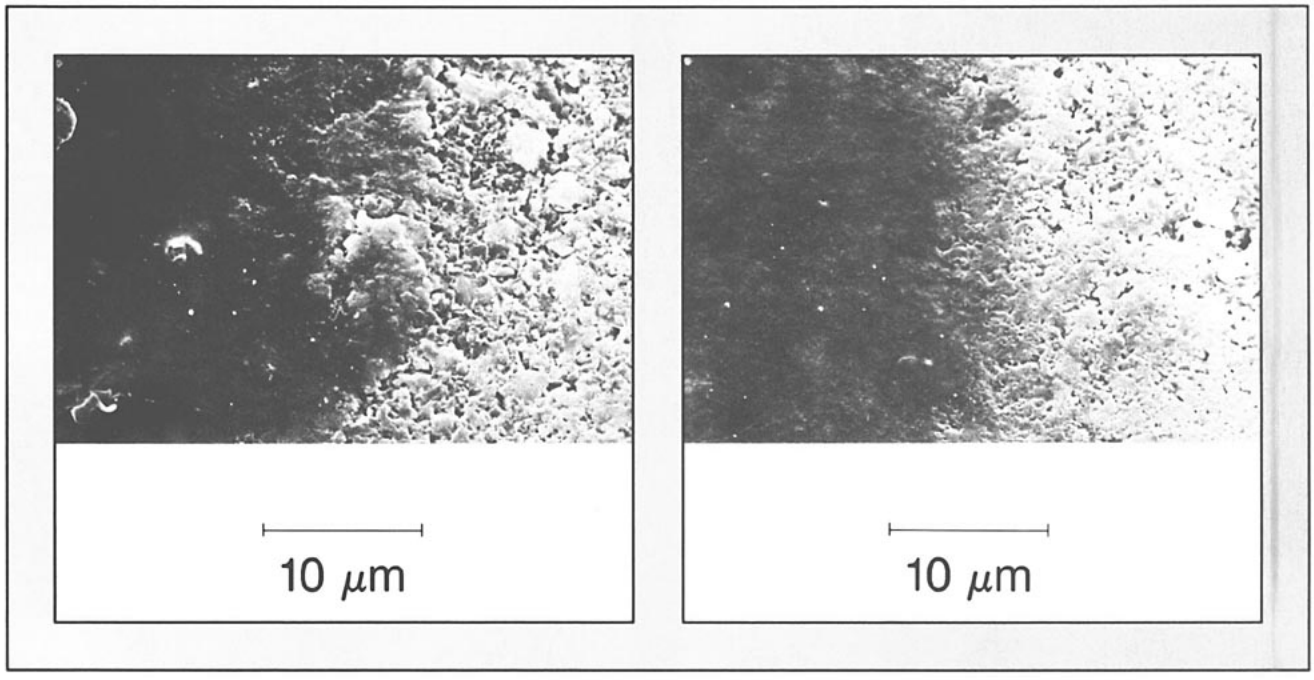
The differences in binder and crosslinking agent proportions can be traced to polysaccharides employed as gypsum stabilizers. **Table XI** lists the test results obtained for the coating color products. This comparison reveals the superior rheology of the test color with a high gypsum content.

The coating colors were processed at a coater speed of 600 m/min; the 2.85-m-wide coater was provided with an inverted blade and with infrared and hot-air dryers. The base paper used was a surface-sized standard web offset mechanical grade of 45 g/m^2 and 6% ash content. To avoid high-viscosity shocks when standard and test colors came into contact, the coating color circuit was thoroughly cleaned between test cycles.

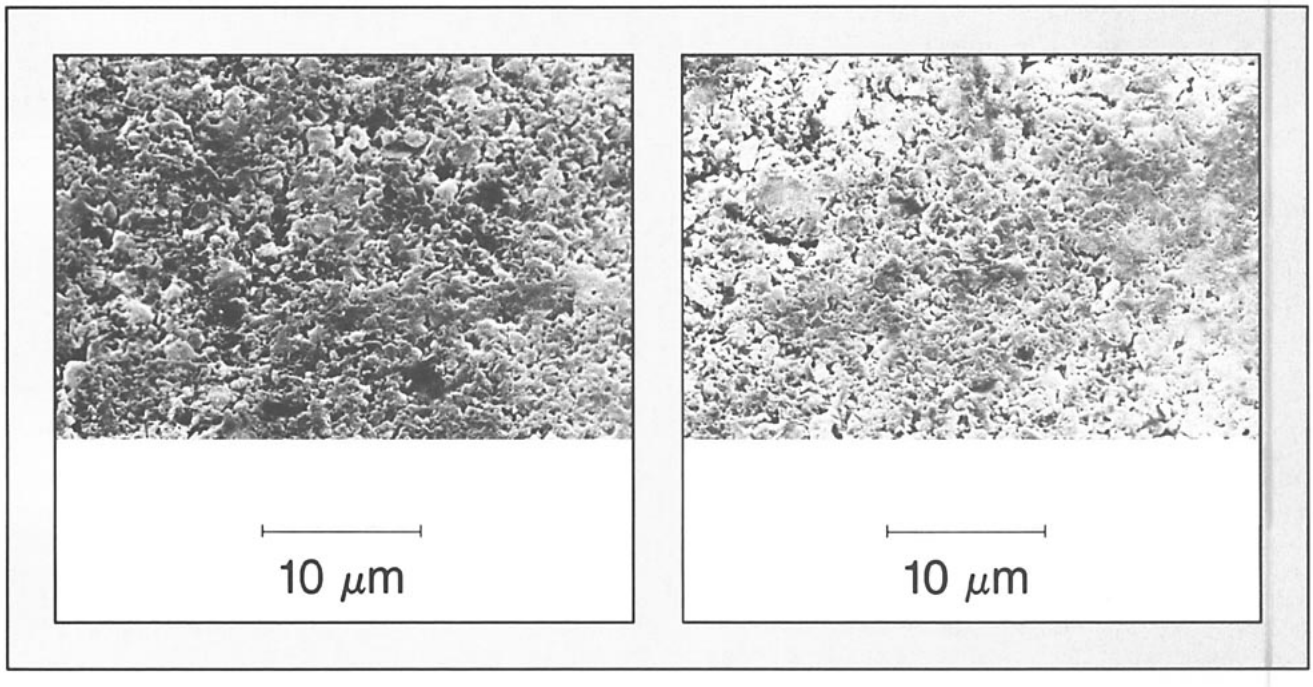
In contrast to the control color, test color processing was accompanied by a drop in blade pressure, which announced itself with low high-shear viscosities upstream. We did not consider this a problem.

As a positive result, constant solids content and blade

6. Field Test 1 printed offset coating color. Left: standard. Right: with gypsum.



7. Field Test 2 rotogravure coating color. Left: standard. Right: with gypsum.



pressures were achieved, which can be explained by high water retention levels. When cutting back over to the standard color system, a pronounced thickening of color was observed in the coater circuit in spite of previous washing operations. The high-viscosity color had to be removed by pressure-feeding large quantities of standard color. In a situation using alternating coater operations, this may give rise to serious production problems.

The slightly lower residual moisture chosen required elevated temperatures and pressures in the supercalender to achieve the target smoothness. The paper end quality shows reduced brightness and opacity values (**Table XII**).

A slight ink repellency observed in the wet pick test and a prolonged penetration time suggest that binder percentages were too high.

In terms of runnability and printability, a mill test print proved equivalent to the control paper with a high $CaCO_3$ content, which was confirmed by SEM photographs (**Fig. 6**).

Field Test 2

Field Test 2 covered split dosage of pigment (*10*). The

problems involved in this mode of operation may be summarized as follows:

- Marked viscosity increase due to kaolin addition, which could not be fully compensated for even with 0.9% doses of polyacrylate as dispersant
- After 1-1/2 reels, we encountered precipitations in the pressure filters, blade stripes, and markings.

Apart from these problems, final quality results were approximately the same as for Field Test 1.

After offset formulations had been developed which allowed high-gypsum colors to be prepared and processed without difficulty, we concentrated our efforts on transferring the experience gained to the gravure sector.

Since coarsely grained pigments have proven satisfactory for high-quality gravure printing, a gypsum with a grain size distribution of 50% (< 2 μm) was chosen for testing. The results of Dixon tests for gypsum contents of 70% and more revealed:

- Superior rheology
- Selection of a kaolin blend offering optimum rheology and printability
- No alkali-swelling thickeners and synthetic binders for improved viscosity
- Declining gloss
- Gravure printability losses
- Opacity decrease.

Field Test 3

Based on these findings, pilot-plant tests were conducted to work out a gravure color system allowing the use of flue-gas gypsum and citric-acid gypsum. A field test was carried out to study the suitability of these formulations under mill processing conditions. Flue-gas gypsum was used for Field Test 3. The test was conducted on a semi-matte product offering good gravure printability (*10*).

Compared to the kaolin color, the gypsum-containing coating color showed a 3% increase in solids at lower high-shear viscosities.

We had no problems processing the coating color in an on-line coater, although solids increased from an initial 65% to 73% due to inadequate water retention.

Supercalendering, however, was another matter. From the third reel, deposits were forming on the rolls at 4% absolute moisture (*10*). As a result of reduced supercalendering effects, opacity values were comparable to the control paper. Coat setting was unsatisfactory, and print qualities turned out well in spite of lower smoothness levels, which were confirmed by SEM photographs (**Fig. 7**).

Summary

Field tests show that hydrated gypsum grades of different origins are suitable for paper coating, giving glossy and matte surfaces for both web offset and rotogravure printing. This statement is valid provided pigment and color systems exhibit a high level of mechanical and chemical stability and, particularly, if pigment blends are used in the color formulations. If we are sure that gypsum and kaolin can be blended and stored at any ratio, color formulations for a broad quality spectrum can be developed without great difficulty. It may be concluded therefore that, despite all the teething problems encountered on coaters and supercalenders, industrial gypsum in its present form is an interesting supplement to a broad range of coating pigments.

A serious impediment to the immediate utilization of larger quantities of this new pigment is the risk of re-precipitation of dissolved calcium sulfate in pumps and pipes of the paper machine circuit. How this problem is addressed will, to a large extent, decide the degree to which gypsum will be employed in the paper industry in the future.

Previous solutions to the problem of recycling high-gypsum waste papers, coating colors, and coating broke by either opening white-water circuits or by fully closing them, have failed to produce the desired results in the majority of applications.

A promising approach would be a controlled modification of the dissolution kinetics by way of adsorption of protective colloids and complex coacervation at the gypsum interfaces.□

Literature cited

1. Huggenberger, L., 1989 PTS Coating Symposium, Paper Technology Foundation, Munich, in press.
2. Clark, D. A., Deutsche Papierwirtschaft (3): 53(1985).
3. Kraft, K. and Huggenberger, L., Das Papier 40(10A): V114(1986).
4. Wirsching, F., Chemie in Unserer Zeit 19(4): 139(1985).
5. Gmelin's Handbuch der Anorganischen Chemie, Teil B, Calcium (Tome 28), Verlag Chemie, Berlin, 1961.
6. Thehrin, A. J. and Thebrin, P. C., Wassrige Aufschlammung von Gips oder Kreide und deren Verwendung zum Beschichten von Papier, Berol Kemi AB, Strenungsund SE, D.O.S., DE 3612087 A1, 1986.
7. Naucollas, G. H., Reddy, M. M., and Nai, F., J. Crystal Growth 20: 125(1973).
8. Wirsching, F., Knopfel, D., and Frank, G., Chemische Technologie—Anorganische Technik II, Gips (Tome 3), Winaker-Kuchler, Carl Hanser Verlag, Munich-Vienna, 1983.
9. Eklund, D., Paperi ja Puu 58(9): 558(1976).
10. Hofmann, H. P., Weigl, J., and von Raven, A., Wochenblatt fur Papierfabrikation 9: 365(1990).

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