Precipitated calcium carbonate

A quiet market expects excellence

by Dr Wilhelm Schober*

Precipitated calcium carbonate has had an eventful life until now. In the seventies, when micronised calcium carbonate (natural dry and wet ground) started to grow enormously, all the precipitated carbonate producers felt the pressure of that cheaper fine mineral and were put in a defensive position. In the eighties the white carbonate filler PCC had found most of its unique positions in branches in which technical facts were dominating and hence a quiet development took place. New applications to paper-production, however, predict exciting future aspects.

Production-chemical expertise required

These products are chemicals rather than minerals, as they derive mainly from the following processes:

- the oldest process of E. Solvay produced PCC as a by-product of Na_2CO_3 production
- today's most common type of process starts from burnt lime, followed by hydration to milk of lime and under very distinct conditions recarbonation (precipitation) forms aragonitic and calcitic types of PCC.
- as a by-product of water-treatment

The different shapes of these modifications offer certain advantages for they allow numerous individual applications. Yet the production of the aragonitic (needlelike, acicular orthorhombic) and the calcitic (barrel shape, hexagonal rhombic) type asks for good know-how to produce a consistently high quality product.

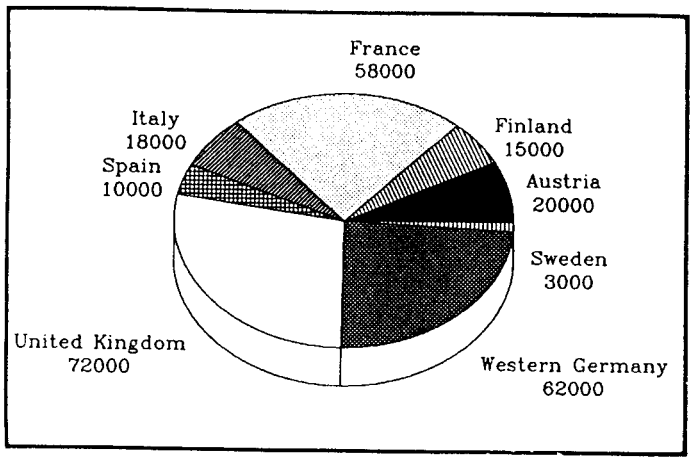
Most of the established companies have historically grown plants and sometimes their competitiveness is weakened by disadvantages in either technical equipment or technology.

A better rentability is given for new sites, but the minimum size seems to be in the range of 15–25,000 tpa taking only the precipitation part into consideration. If a kiln for burning lime has to be included, the demanded capacity will easily increase to 50–60,000 tpa and reach an investment sum of more than DM35–40m.

The limestone may be of medium natural brightness, but it must have a good chemical purity ie. the multivalent metals (Mn, Fe), which lead to less bright precipitates, must be strictly avoided.

Producers — newcomers bother the establishment

The PCC business is in the hands of only a few producers, who try to maintain the status of an exclusive club. But quite recently paper-mills have taken the initiative.



PCC production in Western Europe 1988 (tonnes) (Total production = 260,000)

Solvay — a leading position in Europe

The *Solvay* group, whose production figures have been dominating the European market with a share of about 40%, had an increase of about 20% in the last decade. The production figures have always been kept confidential and the total production of the group is estimated at the moment to be 105,000 tpa.

Solvay produces PCC in four European countries offering good geo-strategic positions. Their goods are marketed under the brandname Socal.

The company's plant in Austria, at Ebensee, runs at a level of about 20,000 tonnes. The local market is important, where Solvay holds a market share of more than 80%. Export figures have not been published. Exports made with Comecon countries can only be estimated and broken down, but seem to be close to 10,000 tonnes. Solvay's market position in Eastern Europe is very strong, as products, such as PVC and soda have been sold there for many years and PCC could be offered beside the others. Their close link to the plastics market is underlined with the stearate-treated PCC types, which hold nearly half of Ebensee's production.

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The German production unit at Rheinberg is estimated to have a capacity of 25–28,000 tonnes. The national market is the main outlet. It has been reported that no stearate treated products are made. Their export rate is estimated at 30–40%.

The French production site at Giraud also produces stearate-coated grades and seems to run on a 45–50,000 tpa scale. Paper, polymers, and plastics are their main outlets. Export rates are estimated at 25%.

The Spanish subsidiary *Docasol* at Revilla de Camargo has an output of 8–10,000 tpa and provides mainly national customers. Here both the paper loading and the polymer segment are of great importance.

Great Britain — also great at PCC

The three UK producers have a long tradition in PCC production. Very early the enormous use of PVC asked for treated grades and two of the producers provide these specialities.

Imperial Chemical Industries (ICI) in Cheshire has an estimated capacity of 40,000 tpa and produces only stearate-coated grades which are marketed under the well known brandname Winnofil. Exports are worldwide and are at about 60–65%. Again the close link to polymers and plastics has dominated the market development of PCC.

The second largest producer *Sturge Lifford* at Birmingham belongs to the *RTZ* group. Its 30,000 tpa production comprises a full product range. Their high-purity and well-positioned treated and untreated grades make them a high quality supplier with worldwide marketing activities. Products are sold under the brandname Calofort and Sturcal. Exports range between 55% and 60%. The production of calcium oxides and hydroxides (approximately 2,000 tonnes) rounds off the company's speciality programme.

Luscombe in London has been producing 2–3,000 tpa of only one PCC grade for some time, exploiting a by-product of municipal water softening. Parts of the plant are being renewed right now; nevertheless they are going to stay at the same capacity. So far its product has been used in toothpaste, pharmaceutical goods, and in rubber and plastics.

The British market in general, however, does not seem to concentrate solely on this order of capacity: quite recently a significant new project (30,000 tpa) was reported to be under consideration in the UK.

Western Germany has alternatives

Besides the above described Solvay activities, *Kalkwerke Schäfer* at Hahnstätten holds an important position in the market. Its main business is to supply the building industry with lime. PCC has been produced since 1954 and it has a capacity of 35,000 tpa. No surface treated products are made. Products are sold mainly to domestic markets. Export activities are targeted at Benelux, France, and Austria and have obtained an estimated share of 20–25%.

The BASF-affiliated fertiliser companies *Chemische Fabrik Kalk*, Cologne and *Gewerkschaft Victor*, Castrop Rauxel produced PCC as a by-product. It was sold to many sectors, especially as a coating pigment to the paper industry. Victor's outstanding service, shipping goods as a high solid content slurry, beside the normal powder-form, is worth mentioning. This 10–15,000 tpa production was closed down quite recently. However, CFK goes on with a modified process and is said to have a 5–7,000 tpa capacity.

Dr Paul Lohmann, a chemicals producer, buys crude PCC and refines it for pharmaceutical applications. Production output varies by demand but does not exceed 1,000 tpa.

Another producer gains importance in France

Scora, a member of the Belgian *Lhoist Group*, produces PCC as a second product of its dolomite operation. The capacity is described as being between 8 and 10,000 tpa. The product is sold under the brandname Scoralite and marketed mainly to the national cigarette paper industry.

A newer pilot plant for special types of PPC is now under order with an output of 1,000 tpa.

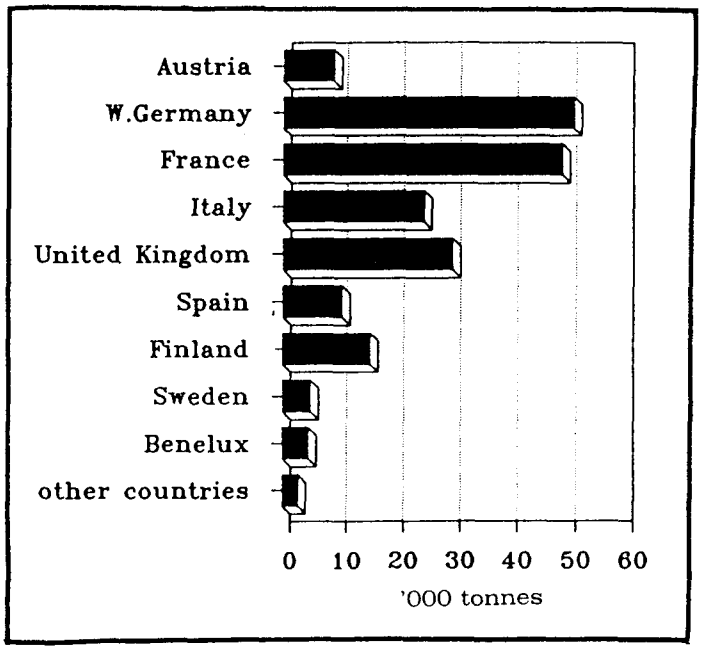
Italy — of small but increasing importance

The Italian producers have smaller capacities, which do not exceed 15,000 tpa in total. *Industrie Chimiche Dr Baslini*, Bergamo has an estimated production of 3–4,000 tpa and *Societa Generale per l'Industria della Magnesia*, Milan is running at a scale of 12–14,000 tpa which, however, is intended to be increased. Both are mainly active in the national market (80%).

Papermills as newcomers

Finland's *Tervakoski mill* has been producing quite a small quantity of PCC for many years. In 1987 the plant was rebuilt to become the first on-site PCC production facility in Europe. All the production is used internally both as a coating pigment and as a filler for TPP (thin printing papers) and cigarette papers(2). The *Partek* group supplies know-how and raw material. PCC production starts from burned lime, which is converted into precipitated carbonate. Today's production is at a level of 15,000 tonnes but will be increased to 30,000 tpa, the nominal capacity of the project.

Lessebo Bruk, Sweden, a smaller speciality paper producer has started a pilot-plant (capacity 3–4,000 tpa designed by *Eka Nobel* in 1987) which is to be the starting point for a further extension to 10,000 tpa.



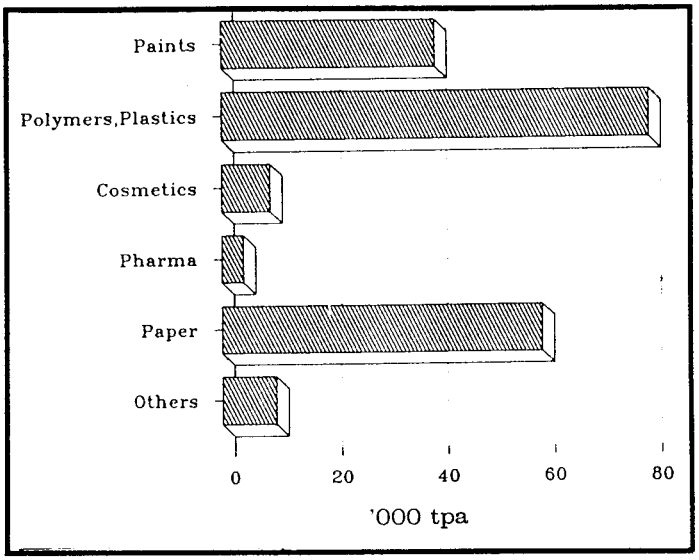
PCC consumption in Western Europe 1988 (European consumption = 202,000 tonnes)

Application technology — the key to success

Nowadays many grades of PCC are available in the market. The differently shaped crystals show quite different results in their end-use. The various combinations of crystal types, stearate-modified grades and the wide range of particle size distributions give a confusing picture to the users. Technical support by the producers and expertise are necessary to use the USPs in the most efficient way.

Paints – the trend calls for PCC
Mixtures of aragonitic and calcitic PCCs have been widely used in paints. The various products are described as follow:

Fineness	5–11m²/g
Average particle diameter	0.2–4 micron
Brightness	97–98 (compared to MgO)
Prices	0.50–0.70DM/kg



PCC consumption in Europe by market sector 1988

The largest sector is emulsion paints, in which a partial substitution of TiO_2 is obtained. Emulsion-paint formulations are quite different all over the world, even inside Europe. Quality levels are different and the formulation criteria are determined by local availability of the commodity fillers.

The British market comprises semi-gloss and gloss paints. They mainly use clays and high rates of TiO_2 (up to 12 and 15%).

Continental consumers prefer semi-matt and matt paints. Their main fillers are carbonates. The rising TiO_2 price and the change to low specific gravity emulsion paints (1.35–1.5kg/l) have forced people to change their formulations over the last few years.

A typical formulation contains a mixture of finer carbonates combined with micronised talc or calcined clay, as a lamellar filler and a precipitated carbonate. The TiO_2 content varies from 0 to 3% in general; only high quality paints show higher values. Under these competitive circumstances maximum dry hiding and sufficient hiding power has to be obtained by cheaper extenders.

These facts appear to be a real challenge to a more imaginative development of PCC consumption.

Today's outlet is approximately 32–35,000 tpa in Europe. West Germany is one of the most developed markets and uses 18–20,000 tpa. The total penetration of the potential market, however, would create demand for approximately double the quantity. We may assume that these trends will spread to other countries and bring about an increase in demand for white ultrafine extenders.

Some more fields of application are:

- industrial and marine paints (chlorinated rubber) where mainly coated types are used (2,000 tpa of PCC are estimated)
- anticorrosive paints
- as a general anti-setting agent in solvent-based paints
- roadmarkings

Quite different features are demanded by printing inks, in which mainly coated and uncoated ultrafine grades are used:

- in letter press inks to achieve long inks
- in litho inks as an extender and for lower wear characteristics

The total consumption of PCC in paints, varnishes, and inks excluding the emulsion paints sector is at an estimated level of 4–6,000 tpa.

Plastics, rubbers, sealants – original markets stable
Extremely fine grades are mainly used for these applications. Products can be specified as follow:

Specific surface	20–50m²/g
Average particle diameter	0.08–0.02 micron
Prices/kg	0.7–1.1DM

In general these ultrafine carbonates do not compete with the bulky CCN. Their main use is linked to PVC polymer. ICI and Solvay, the most important PVC producers, have developed these applications to a high degree.

The use of Ca-stearate, surface-treated PCC has proved important in PVC applications, because agglomerations are avoided and the dispersion properties in the polymer matrix are improved. In general a 2–3% stearate coating is made in the course of PCC production.

The main rigid PVC applications are

- corrugated land drain, drainpipes, guttering
- pressure pipes
- rigid profiles

The ultrafine filler promotes fast gelling of the compound, which improves the extrusion rates. Moreover, the impact strength shows improved performance, reducing breakage during installation and handling. Several users have reported a variety of functions, such as increased gloss finish, reduced plate-out etc.

The trend of PVC usage seemed to decline over the last decade, when competition with other polymers, mainly polypropylene, became stronger and PCC lost some tonnages. But the market share of today's PVC-applications seems stable.

Plasticised PVC, such as cables and coatings (eg. floorings), had been a long term outlet for PCC. Increasing competition has led these sectors to decline.

Technical reasons for the use of PCC have been

- its influence on the rheological properties
- the improvement of scratch resistance.

An enormous and still increasing sector is PVC plastisols. Here PCC is mainly used in automotive underbody coatings and sealants, because rheological and adhesion properties are improved. Yet not all the automotive industry and repairing systems suppliers have changed to the newer plastisol systems and a realisation rate of 50–60% only will give some space for PCC increases in years to come.

European PCC producers have exported about 20–25,000 tpa for the production of polymers and plastics to overseas countries. Sealants for other applications (ceramic tiles, window-glasses etc.) are made from other polymers: eg. silicone or polysulphide. The functions of PCC as a filler are mainly related to its fineness:

- influence of rheological properties (thixotropy, stable viscosity)
- improvement of physical properties (good elongation, low modulus).

In addition PCC is used in 1 and 2-component polyurethane systems, where rheological support, tear strength, and low modulus are noticeable. Loading rates are high and some thousand tonnes are expected to be needed for this end use.

The total consumption of PCC in all polymer and plastics applications in Western Europe is estimated at 75–80,000 tpa. but, COMECON, where PVC still has a strong position, also has an important share.

	consumption (tonnes)
W. Germany	23–25,000
France	15–20,000
UK	6– 8,000
Italy	8– 9,000
Comecon	10–12,000

The importance of PCC in rubber seems limited compared to the aforementioned end-uses. Applications range from tightenings, and flexible pipes, to the not negligible quantity used for hot-water bottles.

Cosmetics — the specialists win

Body- and baby-powder and dentrifice sectors are of greatest importance for PCC. Common specifications of these grades are:

Specific surface	6–11m^2/g
Average particle diameter	0.2–0.4 micron
Brightness	98–99
Prices	0.5–0.7DM/kg

The basic raw material for body-powders in Europe is talc (80%), which is combined with magnesium stearate (10%), PCC (up to 10%) and some odorising additives. PCC improves both the free flow of the powder and its absorption capacity. The UK, as the most important body powder producer and consumer in Europe (60%), was an important PCC user in the past; in the meantime some of the market has been lost against $MgCO_3$, but some hundred tonnes are still needed. The total European market for this sector is estimated at 500–800 tpa.

The interest in dentrifice applications has varied extremely over the last few years. The aragonitic form of PCC (particle sizes of 3–15 microns in diameter, large volume aggregates) guarantees a high liquid absorbency and provides a better stability to toothpaste. Its softness provides low abrasion values and is an important fact. The filling rate rises to 40%.

Gel-toothpastes have given hard times to PCC suppliers in some countries, as no fillers are required. Also fluoride-containing pastes cannot use PCC either owing to chemical reactions (the F– would be bound to Ca++ and lose the active role). Here Ca-phosphate is used. Trends have been varying dramatically all over Europe and do not show any consistent picture: some countries are important gel users (West Germany, Austria), others believe in pyrogenic silica-filled pastes (West Germany); in the UK around 3,000 tpa of PCC are used, in West Germany only 1,000 tpa. Only a few countries have high rates of toothpaste consumption (700g/person per year) but many others have only 250–400g/year. The daily discussions in print and the video media have greatly influenced these tendencies and have led to short term changes in product policies.

Besides these applications many more outlets of PCC are:

- as a filler in creams
- as a perfume carrier in face powders
- as a filler and thickener in sunscreen preparations

The total consumption of PCC in cosmetics is estimated at 6–8,000 tpa.

The improvement of personal hygiene will increase the consumption of toilet preparations and a more active role could strengthen the PCC suppliers' position.

Polishes and cleaning systems — a declining sector with hopes
Because of their softness, medium fine grades (average particle diameter 5–6 microns) are used for window polishes and car cleaning substances. Diatomaceous earth and aluminium oxides are now more commonly used in central Europe, because anionic tensides would react with carbonates.

The development of detergents is providing interesting results for PCC: the ultrafine grades (average particle diameter 0.02 micron, specific surface up to 100m²/g) are used as flocculation aids. Final results and exceptional demand for the speciality PCC grades are expected for mid term periods. Prices will be higher and a price of approximately 1.3–1.5DM/kg is expected.

Pharmaceuticals — purity counts
This highly specialised sector gives a chance only to the best. Chemical purity, which is influenced by the quality of the limestone and the precipitation process, is the main demand. All products must comply with the requirements of the national, European, or US Pharmacopeia, where the purity and maximum trace metal levels are defined.

Calcitic and light aragonitic types are used for higher reactivity, with medium and fine particle size:

Specific surface	4–10, 20–28 m²/g
Average particle diameter	2–16, 0.1–0.08 microns
Prices	0.7–1.2DM/kg

PCC is used in the following applications:
- in antacid preparations as a neutralising agent
- in antibiotic manufacture for neutralisation and as a filtration aid
- in soluble tablets (fizzy tablets) as a buffering and dissolution agent
- as a filler in tablets
- as a Ca-source in tablets (Ca-supplements)

The total market is estimated at 3–4,000 tpa, and the market prices are well positioned and provide good profit margins for suppliers.

Paper — high hopes from overseas
PCC was an important white, fine filler for the paper industry until the early 70s. The natural carbonates had not been ground to such a fine powder with the same cost performance before.

Owing to the enormous technical and application-orientated efforts of the *Plüss Staufer* group, CCN (natural wet ground calcium carbonate) underwent great development in the 1970s. Suitable grades enabled the change to a neutral and alkaline sizing system. Ambitious investment programmes by several companies insured a consistent and constant supply — a vital precondition for the paper industry to switch to a different and new kind of filler and coating material.

This boom has been prevailing in Europe, and further investment programmes by the paper industry are going to keep up the demand for these functional minerals.

It seems that PCC had lost its attractiveness not only for price reasons. Its shipment had been very inefficient in the past. Whereas CCN suppliers offered transport in silo and slurry form, PCC was offered in conventional bags only. Even today consumers of some thousand tons have no chance of receiving PCC shipments to meet the paper industry's standards. Bagged PCC require drying (approximately 18–20% solid content is the process concentration where precipitation is made) which increases the costs substantially and diminishes its competitiveness.

Besides, technical expertise for PCC use in paper applications does not seem to be in the hands of the PCC-producers and obviously there does not exist any basic technical and application-orientated programme.

The traditional market for PCC is the cigarette paper sector, where special functions such as increase of opacity and control of the burning rate of the cigarette are fulfilled by PCC.

Prices for suitable paper-loading grades vary among countries and by volume.

Specific surface	9–11m²/g
Mean particle diameter	0.2–0.3 micron
Prices	0.45–0.65DM/kg

The use of PCC in other fine papers is not very common, but interest is increasing.

Developments in the USA seem to be years ahead. The satellite plants, which were pioneered by *Pfizer*, have taken on an increased importance in the PCC scene; it has been reported, that the tenth on-site plant (3) will start up in 1989. The on-site layout shows synergistic effects and is competitive with other commodity fillers. The high expertise of Pfizer in producing suitable types, starting from rhombohedral calcite crystals to the barrel shape, and knowledge in producing high solid content slurries, enabled this development and brought about acceptance in the market. Pfizer owns and runs these plants and is also active in further product developments.

These activities have not found sufficient response in Europe up to now. The established PCC producers have followed all events with interest and started trials with active papermills; but their input for high solid content slurries and application advice seems to be very limited. The initiative in making the

necessary basic developments seems to lie in the hands of ambitious papermills only.

The CCN suppliers will certainly go on watching all these occurrences with suspicious eyes and argue against PCC and on-site plants with low rentability in Europe.

The technical argument against the transfer of the American experience to Europe runs as follows—

- the ash content of US papers is much lower
- paper is not as white as in Europe
- CCN is more competitive and more easily available in Europe
- coating — slurries must have a solid content close to or >70% which is difficult for PCC
- the rheological behaviour of PCC slurries is different and more difficult to master

But there are also a lot of pro-arguments in favour of PCC since it possesses the following properties:

- has a lower abrasion value, which could be important for copying paper at high speed levels
- has much higher brightness, which is important in times when TiO_2 is short and of extreme price
- gives an excellent opacity and smoothness

These facts cannot be applied by every paper mill, but many of them have taken the initiative and have been checking their circumstances and possible benefits.

German papermills had been using PCC with success for several years. But in 1987 the closure of a by-product PCC plant forced them to switch to the darker CCN grades, because no economical PCC alternative could be found.

The total European market has a consumption of approximately 60,000 tpa.

Estimated consumption of PCC for cigarette and fine papers in 1988 (*tonnes*)

Finland	15,000
France	18,000
W. Germany	7,500
Spain	5,000
Austria	3,500
Sweden	3,000
United Kingdom	2,500

Some papermills have started projects for their own on-site plants.

There is a 20,000 tpa project at an important paper mill in Finland, where mainly coating grades are planned to be precipitated. Substantial projects are being studied in paper mills both in France and the UK.

The price policy has partly been responsible for the poor development and the stagnation of PCC in paper applications. Having only limited or no alternatives cigarette paper producers have teeth-gnashingly accepted this high price policy. Almost all paper mills noted that the prices are too high for increased use. Prices vary between 450 and 630 DM/t free delivered. CCN slurries rank between 200 and 300 DM/t. Many technicians at paper labs, aiming at excellent optical properties and improved paper quality, have achieved technically suitable PCC but they could not justify an increased cost value compared to CCN use. The development of new PCC applications in paper mills has suffered from poor technical expertise and/or insufficient support by the suppliers.

Therefore it is not surprising that paper mills started their own initiatives and projects — excluding the establishment — and are looking for an economical production process and for security in application know-how. In several cases 330–350 DM/t has been defined as a goal, which seems to be a quite workable level.

The future

The importance of PCC will increase and realistic chances of overproportional growth are given.

Counting all the existing on-site plants and new projects, the newcomers are very soon going to take over an important market share. The future prosperity of the PCC-market is about to be promoted and developed by a *mineral using* industry only.

If the basic capacity of an on-site plant is under long term contract with paper mills, it cannot be considered a boldness to introduce its surplus quantity into the free market, which, no doubt, will increase competition. Under these circumstances today's established producers and suppliers will have to fight hard for the driver's seat in this business.

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