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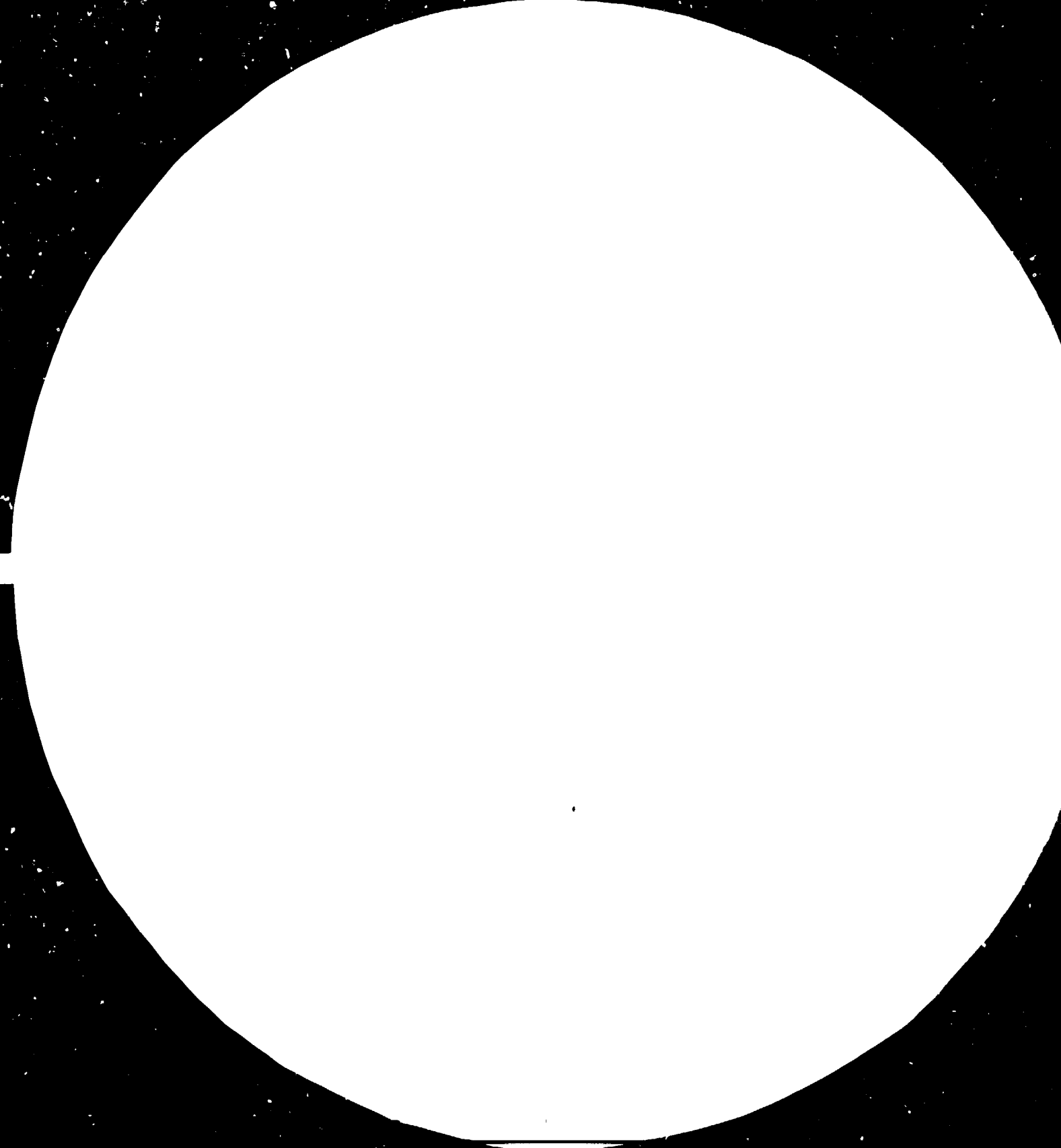
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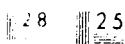
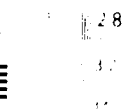
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MICROCOPY RESULTS: TEST CHART

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RECENT ADVANCES IN CRUDE OIL SAVING SYSTEM  
IN PETROCHEMICAL INDUSTRY

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1184

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RECENT ADVANCES IN CRUDE OIL SAVING SYSTEMS IN  
PETROCHEMICAL INDUSTRY

Dr. Jiří E a b ů r e k

Introduction

Problems of Provision of Energy Sources

The problem of fuel and energy is moving, in the present stage of development all over the world, into the forefront of the interests of scientists, engineers and economists. This is natural. On the one hand the consumption of energy is increasing with the progress of the scientific-technical revolution, with the advancing development of production and with the growing number of inhabitants of our planet. On the other hand the sources of energy predominantly utilized in economic practice up to the present are limited and are gradually being exhausted and the provision of new sources of energy is in the stage of research and experimental proving or only of establishment of an economically significant extent of production.

Energy is very expensive at the present time and research of new kinds of energy is considerably demanding and costly so that the problem of energy supply can be solved only in harmony with the development and effectiveness of the whole economy.

In the graph of worldwide electric power generation the beginning of our century is marked by a not particularly prominent dot. In the fifties of our century the curve has reached the value of 1000 milliard kWh per year, in the seventies it exceeded 5000 milliard kWh per year and by the end of this century yearly generation of electric power should exceed, according to UNO forecasts, the level of 30.000 milliard kWh.

An absolute majority of power generated at the present time is obtained by combustion of fossil fuels. Extractable deposits which have been created on Earth in the course of hundreds of millions of years, mankind of the present is capable of burning within two to three centuries. Needless to say, even today organisms are cumulating solar energy. However, according to recent calculations of scientists mankind of today is consuming this potential energy of the biosphere at perhaps ten times the rate of cumulation of solar energy by the action of organisms.

All presently known or, for the time being, only assumed deposits of fossil fuels will apparently be extracted within the next decades or, at the most, centuries. With the advancing years the extraction of them will be increasingly costly and their quality growing steadily worse.

Today none of the fossil fuels is a "clean" fuel. Whatever is being burned in the world today and particularly what will be burned in the next decades is much more valuable as raw material for the chemical industry than as fuel.

The modern world needs energy. More and more energy. The petroleum crisis has clearly shown how mankind of today depends on energy.

The present state, with world production of energy based in a predominant measure on fossil fuels, is no longer tenable for any length of time. There is less and less of them, they are an essential reserve for the chemical industry of the present as well as of the future and the combustion of them more and more heavily pollutes the atmosphere.

And what other possibilities do we have? The petroleum crisis has doubtlessly considerably complicated the work of prognosticators. Fundamental forecasts have recently often changed at monthly intervals, and usually quite substantially. Contrary to the original considerations from the turn of the sixties and seventies the trend of a striking reduction of the consumption of petroleum as a source of energy and a moderate increase of the consumption of coal predominates at the present time.

An advanced fuel for the next decades will be natural gas (this is borne out also by the network of transcontinental gas pipelines the density of which is increasing at a steadily rising rate). A high growth of water power can now already no longer be expected. A source of energy which today appears most promising for the future is nuclear energy. It must, however, be admitted that the present fission reactors on the one hand excessively waste the valuable natural raw material which is uranium, on the other hand (and that applies also to breeder reactors) they produce a large quantity of dangerous radioactive wastes, the problem of a perfect disposal of which remains unresolved so far. It appears that a definite solution of the energy problem will be only a practical mastering of the thermonuclear reaction.

#### Limits of Natural Sources of Raw Materials

The finiteness of our planet is a matter of which already scientists in ancient Arabia were convinced. However, sometimes such is human history that occasionally a very long time passes from the original discovery to a full understanding of certain facts. Not until the advent of the era of cosmic flights were we shown our Earth as a small blue planet, as a cosmic body, gigantic from our point of



view but even so, and that already quite unequivocally, finite. Of everything available to us here there is a limited quantity.

The natural resources of the planet Earth are divided, as a rule, into two groups, i.e. renewable ones and non-renewable ones. Belonging to the renewable sources are air, water and soil and also representatives of life on Earth, i.e. plants, animals and microorganisms. These elements of our natural environment are renewed sometimes in the course of several minutes, in other cases in hours, weeks, years or centuries. These are periods of time measurable, one may say, by human yardsticks.

Non-renewable from our point of view are natural resources which came into being millions and milliards years ago and a possible renewal of which may be estimated to require a period given by the orders of 6-to 9- digit figures. It is precisely among these non-renewable resources that perforce the natural raw materials must appear which, at the prevailing trends, mankind may exhaust soonest.

Growing in strength are the voices of those who assert that the time is approaching when our claims on these resources will exceed our possibilities of discovering and exploiting further deposits of them.

Today we can already calculate comparatively accurately what are the quantities of the individual mineral raw materials which can be extracted by present methods (as well as by the anticipated methods of future years). Today already the consumption of many raw material grows more quickly than the actual population. Every year more people are consuming these natural resources and, at the same time, the average consumption per inhabitant is on the increase.

Abstracting from the specifics of the petroleum crisis of the first third of the seventies and pointing out certain more general features we can imagine, to a certain extent, the reaction of business circles at a time when the exploitable deposits of some of the important raw materials drop below a viable limit.

When a comparison is made of the consumption of petroleum (1972 - power generation, transportation, chemical industry: 2,65 milliard tons) with the reserves ascertained up to the present (in 1970 this was 70 milliard tons, certain estimates of all reserves of the planet go as far as hundreds of milliards of tons of reserves) the present situation does not seem particularly critical. However, with every raw material, one day the moment must perforce arrive when there will be such a shortage of it that it will

threaten the continued development and the functioning of the economy.

Therefore not only possible isolated consequences of such a state must be considered but in particular also combinations of them. In world economy highly complex chains of relations exist the disturbance of a single link of which may lead to an avalanche-like growth of further problems. To be sure, the petroleum crisis in many countries not only developed into an energy crisis and a crisis of the chemical industry (in many countries the production of synthetics dropped sharply) but also worsened the general raw material crisis. Thus, for instance, the shortage of petroleum very quickly raised the price of natural rubber. In that period also the prices of a number of metals reached a record level. Even though there was a certain calming-down of the world raw material market, a return to the prices of 1970 is considered quite illusory.

#### Effect of Development of Thermoplastics Production on Consumption of Fossil Fuels

Only the energy crisis in 1973 and subsequent years forced the plastics industry in economically advanced countries to revise their standpoint in relation to mineral fillers.

It became obvious that the growing claims of industry for synthetic material of a higher strength a higher rigidity, a higher thermal endurance and a lower thermal expansivity and, at the same time, of a lower price could be met to advantage only by the use of high concentrations of suitable types of mineral fillers. There is, in fact, talk of a coming "composite material age".

The petroleum crisis has shown that the prices of polymers produced on a petroleum base have risen much more quickly than the prices of mineral fillers. The quick rise of the prices of polymers produced from petroleum raw material contributed substantially to a quicker introduction of the production of filled polymers.

By the use of high concentrations of fillers the volume of production of polymers can be increased and, at the same time, a number of their properties can be improved. Apart from a reduction of the costs of raw materials other important economic contributions include a cutting-down of the processing cycles due to an improvement of the thermal conductivity as well as a reduction, in final production, of the rate of rejects caused by warpage of the mold for product shaping.

At the present time a majority of polymers does not contain any fillers regardless of the fact that by the use of them production costs could be cut down and the properties of the products improved as well. This situation is caused above all by insufficient information on the part of the technical public and also by a lack of equipment of the works concerned.

Lately significant progress has been achieved in the development of mechanical equipment for the production of composite materials.

According to a forecast published in the periodical Modern Plastics in 1975, an increase, by the year 2000, of the world consumption of fillers by 1300 % is expected, as shown in the following table:

Table 1: Forecast of mineral filler consumption

	Y e a r			
	1975	1980	1990	2000
Fillers, total (thousands of tons/year)	1060	2500	6900	15000
Thereof carbonate fillers	700	1500	3500	9000
Plastics production, total	13000	18000	38000	58000
% fillers in quantity of plastics	8.1	13.9	18.2	25.9

According to the latest opinions it may be expected that the world rise of the consumption of mineral fillers will be much quicker for the following reasons:

1. The rise of the price of fillers will most probably be much slower than the rise of the price of polymers because fillers and their production are not so much dependent on energy and on the decrease of the world reserve of fossil fuels.
2. The number of processors who process composite materials is growing and thus understandably also the knowledge of the properties of the materials. At the same time new machines for the processing of these materials are being developed and used.

Thus, for instance, the prices of polymers have risen in the USA approximately twofold, the prices of fillers by only 25 % to 50 % as shown by the following table:

Table 2: Price rising of thermoplastics and some mineral fillers

	1973	1976
<b>Polymers:</b>		
Polypropylene	370	620
Polyethylene	310	660
Polyesters	440	820
<b>Fillers:</b> CaCO <sub>3</sub> fine	50	65
coarse	18	22
Talc fine	68	89
coarse	40	55
<b>Note:</b>		
Figures in US Dollars/ton		

As regards the range of mineral fillers opinions are not yet quite in accord. The following are considered the most important ones: microground limestone, kaolin and talc with surface treatment by organic compounds or without it.

Very finely ground and accurately sorted calcium carbonate with surface treatment is used primarily for the improvement of the processing properties of thermoplastics (understandably apart from a saving of the basic raw material, i.e. petroleum). As an admixture it improves the thermal conductivity and thus makes possible a raising of the productivity of work during the final processing technologies.

Kaolin, talc, mica and other specially treated mineral fillers make possible, with the application of a suitable surface treatment (by organic-silicon compounds), a marked improvement of the mechanical properties of plastics and, in a number of cases, the creation of a new widely applicable structural material.

In the study of the optimum composition and micro-arrangement of fillers a new specialized branch of science is engaged. It may be expected that, in future, in a majority of cases mixtures of fillers will be used the actions of which will mutually supplement each other.



Feldspar fillers

Feldspar and nepheline are similar minerals and serve the same purposes. They are anhydrous, alkali alumino-silicates having excellent chemical resistance and are offered in coarse to medium particle sizes. As low surface area fillers, their uses are comparable to calcium carbonate and silica but they are more versatile.

Advantages in plastics are:

Transparency to translucency in most polymers,  
ease of wetting, dispersing and deairing,  
little to no effect on promoter, accelerator or additive activity,  
low viscosity and high mobility at high concentrations,  
less color pigment required to obtain a given intensity,  
improved chemical, weather and abrasion resistance,  
suitable for use in compositions contacting food,  
not a health hazard as a dust or when ingested.

Disadvantages are:

coarser particle sizes are somewhat abrasive,  
settling in low viscosity systems.

As a class, these minerals comprise the tectosilicates, which constitute 75 % of the earth's crust. Granite and associate formations are the most common rock-forming agents.

Feldspar and nepheline are closely associated, the later being classified as a feldspathoid because it was formed from a silica deficient magma or molten rock. The primary difference between the two materials is the ratio of silica to alumina in their analyses. This is of no consequence in their use as fillers.

As with all silicate minerals, the elements exist as atoms bonded with commonly shared oxygen in the crystal lattice. Except for isolated defects and at broken bonds, the elements and their ions are not available for chemical reaction unless the structure is dissolved or otherwise decomposed. Minerals of this class are highly resistant to chemical reactions under conditions much more severe than polymers are able to withstand. The pH of feldspar depends on the exposed surface since fracture occurs at the weakest bonds, the sodium, potassium, and calcium oxide bridges in the crystal lattice. The exposed ions bond with (chemisorb) hydronium ions of water to yield free hydroxyls and thus a basic pH which increases, as the particle size decreases. Whereas feldspar cleaves along planes at nearly right angles to each other, nepheline cleaves predominantly along a crystal plane exposing the alkali oxide bonds. Nepheline then, has a more nearly constant effect on pH over a wide range of particle sizes. The potassium and sodium feldspars, as single species, are very resistant to acids, whereas the calcium type is not.

The commercial mineral is a solid solution called anorthoclase, predominating in the properties of the former.

Nepheline is derived from the Greek word meaning a cloud since the crystals become cloudy when immersed in 10 % hydrochloric acid. The greater numbers of exposed cation sites make nepheline somewhat less acid resistant than feldspar. Both minerals have a very high order of resistance to alkali.

Neither commercial product is a single species of mineral, but there are solid solutions. As such, they do not cleave regularly but fracture irregularly. The particles produced by grinding may have only one characteristic similarity to the pure mineral. For feldspar there is always one 90° angle giving rise to blocky or splintery particles. Nepheline syenite tends to cleave along parallel planes and the particles appear to be splintery or irregular with the flat facet. Both product lines have a minimum of 0,5 µm particles because of the expense of grinding these tough materials.

The Mohs hardness values are relatively high. As the particle size is reduced to below about 5 µm, both feldspar and nepheline syenite reveal a more regular, blocky shape with fewer sharp-edged particles and therefore considerably reduced abrasiveness.

These minerals are among the lowest surface area types because of their particle shapes and low fineness content.

The oil absorption test measures the packed volume of filler particles. Since very low concentrations of fine particles are present, these fillers provide highly packed systems when combined with fine to very fine fillers and pigments.

Feldspar has somewhat better electrical properties than nepheline syenite, but poorer than mica. Feldspar is especially suitable where high concentrations of filler are used to obtain surface resistivity. Dielectric strengths for feldspar in epoxy and polyester compounds are equal to or slightly lower than silica. Conductivity bridges on the particles due to sorbed water, crystal defects, or contaminants, such as black iron oxide in nepheline syenite, are responsible for electrical conductivity and are frequently grossly influenced by the polymer and its ability to bond to the filler surface or to passivate certain conductive sites.

Thus, pure potash feldspar provides excellent electrical resistance in ceramic compositions where the matrix is a glass and no surface sites exist to provide electrical conductivity.

Silicate minerals are non-conductors, so the degree of electrical resistance is largely a matter of purity rather than differences in mineral types.

Thermal conductivity for these minerals is in the range of 5,6 - 8,2 g.cal./sec.cm<sup>2</sup>/°C/cm compared with values of 0,2 - 0,5 for plastics, and therefore they are considerably more conductive than plastics. Specific heat values are about 0,21 g.cal./g/°C for both fillers versus about 0,3 - 0,5 for most plastics. On a volume basis (specific heat density) the fillers have higher values than plastics. On a volume basic (specific heat density) the fillers have higher values than plastics.

One of the primary advantages of these fillers is their mean refractive index of 1,53. Since these minerals wet and disperse readily, their surfaces are quite well contacted by the polymer. Most polymers have refractive indexes near 1,53 so filled compounds may obtain clarity or translucency not provided by other fillers. No other fillers provide this degree of light transmittance at equivalent concentrations.

### Applications

In both dry-blending and liquid mixing with thermoplastics, it is preferable to add these fillers last. They do not agglomerate as fine fillers do and they wet and disperse very readily, so adding them last reduces abrasion or over-mixing in liquid dispersions which may result in excessive air entrainment.

These fillers have been used in all methods of liquid and melt processing. Depending on the section thickness or degree of work involved, all grades may be used. For high-shear melt processes, the finest grades are more suitable (as an injection molding) where minimum abrasiveness is required. Both filler types exert minimum effects on melt-flow or viscosity compared with other fillers having about the same particle size distributions.

Feldspar and nepheline syenite produce the same effects on physical properties and are superior to equivalent particle size calcium carbonates. Abrasion resistance is materially improved by these fillers provided that the polymer bonds adequately to the filler surface and has a moderate to high tensile strength. Highly plasticized or weak matrixes (Polyethylene, for example) do not have sufficient bonding and tenacity to prevent the filler particles from being dislodged.

As with all filled composites, stresses in the matrix are magnified, resulting in reduced physical properties and, particularly, impact resistance. Inherently tough or rigid matrixes are less affected, especially if the fines fillers are used. Strain whitening is also more noticeable with these fillers due to the clarity imparted.

Optical effects are very positive. These fillers transmit radiation from 0,3 to 1,5  $\mu\text{m}$  wavelength. A small proportion of ultraviolet is absorbed and the remainder transmitted, therefore UV adsorbers are effective. Infrared is largely transmitted by the fillers so that heating for vacuum forming of filled sheets is more rapid than with the unfilled sheets.

Thermal stability is positively influenced due to feldspar addition. Although the improvement is partly due to dilution of the plastisol by the highly purified filler, bonding of the electronegative chlorine at cationic (positive) sites of the filler surface reduces the chlorine mobility and therefore polymer degradation.

As with all fillers, polar polymers such as ABS, EVA, nylon, urethanes etc., are most amenable to being filled, with resulting improvements in modulus, flexural strength, and deflection temperature. Bonding such as the silane

coupling agents are effective with both feldspar and nepheline syenite to increase tensile strengths compared with untreated filler, but always at the expense of elongation.

Unsaturated polyester compounds, such as SMC and BMC are highly filled to reduce shrinkage on polymerization and to increase moduli. Both fillers provide the high concentrations required with such compounds, especially in conjunction with finer fillers and pigments, to yield more uniform moulded parts, considerably better weather, abrasion, and chemical resistance, and savings in tinting costs compared with the more commonly used calcium carbonate fillers. Other benefits are exceptional ease of dispersion and de-airing, no effect on promoter or accelerator activity, excellent flow, molding and mould detail properties, and show-through clarity where it is desired to see the fibrous reinforcement distribution. The same benefits are imparted to matched metal die molding, sheet moulding gel coats, filament winding, and casting of the filled compounds.



Silica fillers

There exist at this time as many as 22 distinct phases of silica and each one of the phases is chemically  $\text{SiO}_2$ . Currently, not all of the phases are useful in plastics but a number of them are. Interestingly, the various phases, and even phase variations, offer distinct advantages and disadvantages. For example, a synthetic colloidal form of silica under the amorphous phase offers the great surface area, thixotropic effect and distinct reinforcing properties. Polymers filled with this form have greatly increased viscosity which may result in processing difficulties. There are flocculated varieties of the colloidal form which give flattening characteristics and composite properties somewhat different from the particulate colloidal phase. Moreover, the synthetic forms just mentioned are so fine in particle size, they offer little in the way of hardness in finished composites. They lack the purity and "anhydrous" characteristics that some of the naturally occurring, low quartz varieties offer.

Natural silica products in the low quartz phase come from quartzite and the tripolitic forms, which would generally be termed natural, microcrystalline quartz. These forms of silica are usually less expensive than the synthetic, colloidal forms.

They too, have advantages and disadvantages. These low quartz varieties offer much lower surface area, hence better rheological flow. Excellent electrical insulation, heavier loading potential, creates purity, and good mechanical properties are other benefits. The drawbacks would be increased wear of processing equipment due to hardness of this filler, and the lack of reinforcing properties because of lower surface area.

Diatomaceous silica is very high in  $\text{SiO}_2$  content. Quantitatively, the silica content will range about 90 %. Other constituents comprising the remaining 10 % are  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ ,  $\text{CaO}$  and  $\text{MgO}$  and some others.

The uncalcined variety contains up to 4 %  $\text{H}_2\text{O}$  while calcined varieties have about 0,5 %. Uncalcined diatomaceous silica has a rather high surface area of  $15 \text{ m}^2/\text{g}$  while the calcined grades measure  $3,0 \text{ m}^2/\text{g}$ . Oil adsorption is quite high, from 90 - 150 %. The effect of diatomaceous silica on processing and composite properties is somewhere between synthetic amorphous silicas and naturally occurring types. The diatomaceous silica particles have a highly porous structure, and the phase of silica is micro amorphous and opaline silica.

Fused silica is manufactured by subjecting high purity quartzite to temperatures in excess of 4,000°F. Finely divided fused silica has a coefficient of thermal expansion in the range of  $0,54 \times 10^{-6}/^{\circ}\text{C}$  from 0 to 1,000°C. This low thermal expansion is very desirable in composites subjected to wide variations in temperatures.

All of the silica materials discussed are in adequate supply based on current demand. The synthetic, amorphous silica material prices vary widely. The reasons for difference in price range are degrees in fineness and purity. The naturally occurring quartz phase material is cheaper than diatomaceous silica or fused silica.

Surface modification via the hydroxylated surface of silica is a subject of wide interest. Silanol activity on the various phases is believed to vary due to origins. However, surfaces can be modified to offer organofunctionality, hydrophobicity and non-functionality. Commercial activity in surface modification is limited now, but the future will call more and more for functional particulate silica materials with the interface tailored to a specific end use.

A dramatic source of silica of the opaline variety will come from rice hulls.

Rice hulls are about 15 to 25 %  $\text{SiO}_2$ . The hulls have been an environmental burden and waste product over the years. This fascinating source of silica is under the careful study and recent developments should provide a variety of silica based products. The lower index of refraction and other unique opaline silica properties from plantlife origin will be serving an unfilled need in the plastic field.

The two broad areas of usage for pyrogenic silica are in rubber and plastics. The advantages offered by the use of pyrogenic silica are primarily the following:

- in thickening and thixotropic effect for liquids,
  - its effect as an antisedimentation agent,
  - its reinforcing effect in elastomers,
  - as an antiblocking agent in plastic films,
- and good dispersibility under many applications.

The silica particles have silanol groups in their surfaces while Si-O-Si bonds are located inside these particles. Development of the silanol groups is attributed to incomplete condensation during the silica process. The SiOH groups on the surface of adjacent particles have a strong tendency to interact with others through hydrogen bonds.

As a result, a three dimensional lattice structure composed of silica can develop, and this produces an increase in viscosity in liquid system. These relatively weak hydrogen bonds break down as even light shear forces are applied. Aside from increased viscosity and thixotropy, the silanol groups are reactive sites for surface treatment. Silanes are used to render silica hydrophobic, and are conceivably organofunctional via ambifunctional silane coupling agents.

Diatomaceous silica is a naturally occurring opaline phase of silica. The ore is actually the skeletal remains of plankton. The variety of shapes is a world of fascination under the microscope. Diatomaceous comes from the word diatom, which is a single celled aquatic plant.

#### Calcium carbonate fillers

Calcium carbonate fillers have relative high volume usage in plastics, due to their unique advantages, including the following:

- their costs is among the lowest of all the mineral fillers,
- they are nontoxic, odourless,

- they are white with low refractive index, easily colored to any desired shade,
- their softness
- their dryness - no water of crystallization,
- the particle sizes available - perhaps the widest range of all fillers,
- particle size distribution is controllable for optimal packing in each polymer system,
- they are easily mixed into formulations, sometimes aiding the mixing of other ingredients,
- they are anti-plate-out agents, exerting mild scouring action during processing,
- they are acid acceptors, for secondary stabilization of PVC, neutralizing chloride ions,
- they reduce shrinkage during molding and curing, as in unshrinkable reinforced polyester sheet molding compounds,
- they are stable over a wide temperature range, converting to calcium oxide (CaO and carbon dioxide/CO<sub>2</sub>/ between about 800-900°C).

Calcium carbonate is a polar, reactive substance, having several possible advantages for plastics use:

- a/ when attacked by acids, CO<sub>2</sub> is evolved and soluble salts are formed. Many plastics, such as epoxy bind CaCO<sub>3</sub> so that compound, even though highly loaded, resists acid attack.

- b/ When heated between about 800-900°C, CO<sub>2</sub> is evolved and CaO is formed.
- c/ In polyethylene and polysterene, CaCO<sub>3</sub> loading tends to cause embrittlement; however copolymers, cross-linking agents, film grades, and coupling agents are available to permit succesfull loading of polyethylene. Impact resistant grades of polysterene can be loaded with CaCO<sub>3</sub>.
- d/ The trigonal shape of crystals CaCO<sub>3</sub> provides little reinforcing action, compared to strongly reinforcing materials as glass fibres, asbestos etc.
- e/ In polypropylene, talc, and asbestos fillers have higher stiffness, flexular modulus, and deflection temperature than calcium carbonate; however calcium carbonate in polypropylene has better impact resistance, possibly due to better bonding between polymer and calcium carbonate.
- f/ Drying of calcium carbonate may be needed for moisture-sensitive applications, since the moisture content of purified calcium carbonate is usually about 0,06-0,20 %.

Calcium carbonate contrasts sharply with other high volume fillers such as clay, talc, silica, silicates and asbestos, which may be much darker in color, stiffer in filled plastic compounds, and, in the case of silicates and clays, results in a more expensive product.

Beneficiated  $\text{CaCO}_3$  description: pure, soft, white, powder, low costs, abundant, remains flexibility of plasticized PVC, yet maintains stiffness and surface smoothness in glass-reinforced polyesters.

Important manufacturing processes for  $\text{CaCO}_3$

Purified Ground  $\text{CaCO}_3$

This type has a highest usage for plastics, because it is purified by removal of iron and silica to minimize degradation of plastics, and ground fine enough to provide sufficiently high physical properties of filled plastics at lowest possible costs. The calcium carbonate is white with a fairly low refractive index, and all colors, from white plastics with  $\text{TiO}_2$  to black plastics with carbon black, can be produced with minimum interference from  $\text{CaCO}_3$ .

Crushing in gyratory crushers or jaw crusher or roll; large lumps are crushed to pass through 3 inch mesh.

Disintegrating proceeds in crusher, rotary hammer mill or stamp mill, ring-roll mill, pebble mill, or edge runners to pass through 100 mesh screen. Flotation removes impurities. Wet or dry grinding (example-pebble mill) is autogenous or with grinding media.



Carefully controlled classification, solids separation, drying and micronizing steps, result in a medium particle diameter of about one to 10 micrometers. Micrometer is usually abbreviated " $\mu$ " or "micron".

Dry processed coarser  $\text{CaCO}_3$

For some applications, such as vinyl foam carpet backing and inexpensive dark floor tiles, fairly coarse unpurified  $\text{CaCO}_3$  is used. Processing is simple, consisting of crushing, disintegration and pulverizing, followed by "air separation" i.e. removal by centrifugal separation of oversize particles by the counteraction "Whizzer" or multivane "deflector".

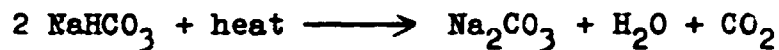
A typical example of processing might consist of a jaw crusher, a rotary hammer mill and a Raymond suction mill with dust collector and vacuum exhauster.

Finest grain: about 12  $\mu$  median diameter

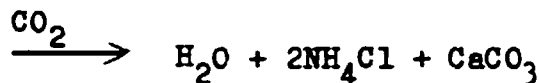
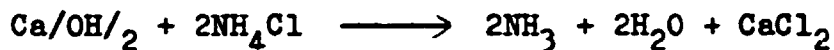
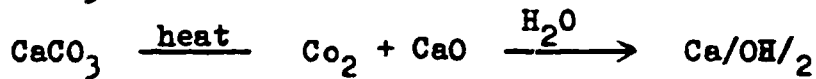
Properties: unpurified, coarser, wide size distribution, color varies with feedstock.

Precipitated calcium carbonate

Ernest Solvay, a Belgian, in 1864 successfully manufactured  $\text{Na}_2\text{CO}_3$  by an ammonia process:



$\text{CaCO}_3$  is used in this process as follows:

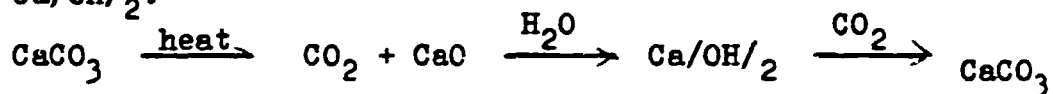


Naturally occurring  $\text{CaCO}_3$  is a starting material and in this process precipitated  $\text{CaCO}_3$  is a by-product. This is also the case in the NaOH and recarbonation process described in the following sections.

Production of the by-product is limited by amount of main product produced. Precipitated  $\text{CaCO}_3$  is washed to remove soluble salts, then dried and micropulverized. The particle size is controlled by conditions of precipitation: temperature, concentration, rate and order of addition of ingredients and amount of agitation. Particle size are fairly uniform and can be varied from about 0,03 to 0,05 up to about 8 - 10  $\mu$ .

Impurities are NaCl and water. Precipitated  $\text{CaCO}_3$  is used in specialized applications where purity, fineness, uniform particle size and excellent whiteness justify their higher cost.

Precipitation  $\text{CaCO}_3$  by recarbonation consists of heating  $\text{CaCO}_3$  to form  $\text{CO}_2 + \text{CaO}$  that is reacted with water to form  $\text{Ca(OH)}_2$ . The  $\text{CO}_2$  is saved and recombined with the  $\text{Ca(OH)}_2$ :



The product is aragonite, with higher sp.g. than calcite. Median particle sizes are between 0,2-2,0 and particle size distribution is wider than the previous precipitated material. Advantages of precipitated  $\text{CaCO}_3$ : high purity grades for food contract uses, very fine particle sizes for high viscosity non-sag plastisols and polyesters. Disadvantages: higher cost, higher energy to manufacture, ionic and water content must be taken into consideration, fineness causes excessive viscosity in some polyesters.

#### Surface coated $\text{CaCO}_3$

In general, calcite coated with stearic acid, calcium stearate and others have improved rheological properties, with little improvement in physical properties.

Commerially, calcium carbonate coated with stearate are used in some plastisols and rigid vinyl compounds.

Properties of calcium carbonate

Calcium carbonate is an abundant material, so stable that entire mountain ranges and coral and mollusc shell portions of seashores are composed of  $\text{CaCO}_3$ . In living organism- from simple seashells, coral and mollusks, to the most highly advanced vertebrates structures containing  $\text{CaCO}_3$  furnish defense and support and contribution to motion and veverage. Skeletal structures, containing calcium phosphate and  $\text{CaCO}_3$  outlast all other body parts.

In nature, when the calcium is dissolved by diferent solvents, eventually the dissolved calcium combines with carbon dioxide to form the stable calcium carbonate again.

Unique features:

- a/ An index of refraction close to that of many plasticizers and resins leads to minimum intereferece with colorants,
- b/ acid acceptor serves as secondary stabilizer in polyvinyl-chloride-PVC,
- c/ purity in some grades for USP, FDA, food contract applications,

- d/ temperature stability up to about 550°C,
- e/ wide range of particle sizes and distribution available,
- f/ readily coated for improved melt rheology when needed,
- g/ retards smoke formation when PVC compounds are heated.

Table 3: Physical properties of calcite, aragonite, dolomite

	CaCO <sub>3</sub> calcite most stable form	CaCO <sub>3</sub> aragonite converts to calcite	CaCO <sub>3</sub> .MgCO <sub>3</sub> dolomite /45 % MgCO <sub>3</sub> by wt/
specific gravity	2,60-2,75	2,92-2,94	2,80-2,90
hardness/Mohs/	3,0	3,5 -4,0	3,5 -4,0
melting point	1339°C 1025 atm. decomp. 900°C	decomp. 825°C	decomp. 730-760°C
solubility in aq.CO <sub>2</sub>	100 times above	100 times above	100 times above

Beneficiation methods for calcium carbonate fillers have been evolved and are being improved for the removal of impurities, particularly ions that would interfere with electrical volume resistivity, as well as iron and silica.

The calcium carbonate filler industry has designed fillers to meet requirements for each major use. Some examples are listed below:

1. Electrical PVC wire coating type filler shipments are specifically controlled for low ionic content, and checked by making a standard compound and measuring electrical volume resistivity.
2. Glass fiber-reinforced sheet molding compound filler shipments are controlled for low and uniform polyester viscosity.

Future developments will be pointed directly to each use. Particle size and distribution may be tailored for best performance in each process. Coating, when needed, will help rheology requirements for easy processing with optimal production rate using minimal power.

#### Current applications

The highest volume uses for beneficiated  $\text{CaCO}_3$  are for flexible PVC compounds, plastisols and glass-reinforced polyester compounds. Filler level for flexible PVC is usually in the range of 20-60 phr of  $3\frac{1}{2}\mu\text{m}$   $\text{CaCO}_3$  (phr = parts by weight of ingredient per 100 parts resin by wt).

Many examples of filler loading vs physical properties are published in trade and technical literature of PVC resin manufacturers and PVC stabilizer manufacturers and in books on PVC technology and plastics.

Finer fillers cause less of a decrease in physical properties in the same loading, while coarser fillers cause problems in thinner calendered films and coatings. Adequate physical properties at lowest cost per unit volume influence choice of filler and loading.

PVC plastisols and organosols - here is  $\text{CaCO}_3$  loading usually 20-100 phr, particle size is usually between 3-15  $\mu\text{m}$ . A wide range of particle sizes are used in this area: from coarse calcium carbonate in PVC carpet backing and mechanically frothed PVC foam cating under PVC tile, to ultra-fine precipitated  $\text{CaCO}_3$  and coated chalk which control the thixotropic viscosity of sealants. Coarse particles lead to lower viscosity plastisols, but the coarser particles may form a sediment during storage and cause handling problems.

At present, a main large use for rigid PVC is in pipe and conduit. Currently 0-5 phr, 2-3  $\mu\text{m}$  calcium carbonate filler is used in potable water pipe (in a future possibly up to 40 phr).

PVC floor tiles are sometimes called "asbestos floor tiles" because the darker colors may contain asbestos as one of the fillers. Calcium carbonate loadings of about 80-400 phr small granular size are usual, with total filler loadings up to about 500 phr.

Low density polyethylene and high density polyethylene can be successfully loaded with ground calcite. Considerable effort has been devoted to finding ways to increase the physical properties of loaded polyethylene. Successful solutions to the problem are as follows:

- a/ co-polymerize polar groups in the polyethylene, such as vinyl-acetate groups, ethyl acrylate groups or carboxylic acid groups,
- b/ cross link the filled polyethylene with an organic peroxide, that is "cure" the polyethylene, making it a "thermoset" material.

High density polyethylene can be cross-linked as well as low density polyethylene. Blends of low density polyethylene with ethylene-propylene-diene rubbers are readily cured with organic peroxides.

- c/ Coat the calcium carbonate with a material having both polar groups and hydrocarbon chains, or with a carbonate xylated polyolefin.

These methods are in development.



Both propylene homopolymer and copolymers are readily accepting calcium carbonate of 3 $\mu$ m particle size at loadings of 30-40 % of the total formulation (that is, about 43-76 phr CaCO<sub>3</sub>). For example, automotive panels use 35-40 % filler, about 30 % filler is used in polypropylene "paper" that absorbs and retains the correct amount of ink when printed.

Calcium carbonate fillers are used to some extent in polyurethane foam, epoxy compounds, and phenolic resins. In polyurethane foam, the CaCO<sub>3</sub> particles serve as nuclei to produce a uniformly small cell size. Epoxy potting compounds with calcium carbonate filler are well known. Acid-catalyzed phenolic resins are not suited to CaCO<sub>3</sub> filler; only alkaline types of phenolics can be filled with calcium carbonate.

Limestone filled polypropylene is one of the most recent plastics materials. Although it may be sound to be little more than a minor extension of the existing types of filled polypropylene, it is in reality totally new material with properties which extend the performance of polypropylene into the areas of ABS and other high cost plastics.

The major features of limestone filled polypropylene are: high stiffness, ease of processing, low cost, improved temperature performance over virgin polypropylene, reduced cycle times, natural matt finish. The compound being introduced is already arousing substantial interest, especially in the automobile industry. However its combination of properties and economy are likely to lead to its rapid introduction in many industries, especially as an ABS replacement.

Polypropylene has been widely described as the polymere of the future, and has been predicted as having the fastest growth rate of any of the major polymers. This prophecy has been backed by many of the major plastic producers by installation of new polypropylene polymerisation capacity, and is therefore likely to become self-fulfilling. New capacity for polypropylene in Europe recently installed, being commissioned, or announced, approaches some 1.000.000 t/year. This predicted growth will only be fully achieved by increasing the range of applications of polypropylene, and in many instances it will require modification of the polymer to increase its range of technical performance. This modification will include compounding polypropylene with other polymers, elastomers, fillers, reinforcements etc., and combinations of these.

One result will be to increase very substantially the proportion of plastics used in fully formulated form as opposed to natural polymer. This will emphasize the growing importance of the speciality plastics manufacturers in the materials supply chain.

Polypropylene has many technical advantages, including ease of processing, low density, reasonable temperature performance, good chemical resistance and high toughness and ductility, especially in copolymer form. It also has the commercial advantages of low cost and ready and stable availability. Polypropylene, however, has some technical disadvantages within its field of application, in particular low stiffness. In addition, its sharp melting range and low melt strength limit its application in such areas as thermoforming and blow moulding.

The stiffness of polypropylene can be substantially improved by compounding it with fillers. Almost any filler will improve the stiffness of polypropylene, but fibrous fillers such as glass and asbestos, or platelet shaped fillers such as talc or mica have a particularly good stiffening effect. Such offset the advantages of improved stiffness and heat distortion temperature by reduced impact strength. This is illustrated in Table 4, which compares properties of various filled polypropylenes with flexural modulus used as a measure of the stiffness of the material.

This table also includes for comparison a chalk filled polypropylene. Because of the more nearly spherical particle shape, the degree of reinforcement is less than for anequal filler loading of talc, but the effect of impact strength is not so severe. All this mineral fillers have the additional advantage of reducing the shrinkage on moulding compared with unfilled polypropylene, and increasing thermal conductivity, which leads to faster cooling rates and hence reduced cycle times and improved moulding performance in injection moulding.

Table 4: Properties of various filled polypropylene

	Heat distortion Temp. °C 1,82 MN/m <sup>2</sup>	Flexural Modulus GN/m <sup>2</sup>	Notched Impact Strength J/m
GP moulding rate unfilled PP co- polymer	55	1,38	147
20 % talc filled copolymer	70	2,75	36
40 % talc filled copolymer	76	3,73	31
30 % coupled glass fibre filled copolymer	155	5,50	212
40 % limestone filled copolymer	73	2,82	41

Limestone, as said before, is chemically almost identical to the ground chalk (whiting), marble and calcite fillers currently in use. However, it offers the advantage of even better retention of the <sup>b</sup>asic toughness and ductility of the polypropylene polymer and the ability to use even higher loadings.

A properly formulated filled compound, however, will contain small proportions of other additives to aid processing and ensure the full development of physical properties. This will produce a considerable additional boost to physical properties, particularly impact strength, as illustrated in Table 5 which compares the properties of simple 50 % limestone filled copolymer with a properly formulated sales grade of the same filler content and same base copolymer.

As can be seen, limestone filled polypropylene compounds with filler contents as high as 60 % can be used. Where optimum physical properties, and in particular high quality of surface finish on an injection moulded item, are required, it is recommended that a lower filler level, up to a maximum of 50 %, be used. Even at the lower filler levels, limestone based compounds show considerable advantage over other mineral fillers, particularly in impact strength.

Table 5: Comparison of different limestone filled copolymer

	Simple 50 % limestone (50 % polypropylene compound)	Fully formulated 50 % compound LPC 5004
Melt flow index	3,0	3,0
Tensile strength	23,0	23,0
Elongation at break	43 %	52 %
Notched impact strength KJ/m	55	90
Flexural modulus	3,16	3,37

A range of physical properties is compared with limestone, talc and ground whiting at 20 % filler content in Table 6. The impact strength performance is particularly marked. Unfortunately any modification such as with limestone filler produces disadvantages as well as benefits. The natural colour of high limestone content compounds is a pale straw, and such compounds are obviously opaque. This limits the colour range which can be produced. High gloss finished cannot be achieved on highly loaded compounds, on the other hand, the filler has a natural matting effects and a range of surface finishes from flat matt to silk sheen can be readily achieved.

The filled compounds have a substantially higher specific gravity than unfilled, and account must be taken of this in considering the economics of the system.

Ground limestone is a relatively low cost material, approximately one tenth the cost of polypropylene by weight. Even allowing its high specific gravity, much lower in cost than polypropylene in volume. It is unsuitable, however, to sand the raw filler to the granules in an injection moulding machine or extruder, except for low loadings in specialised equipment. To benefit from its desirable properties it must be properly formulated and compounded.

Table 6: Physical properties of polypropylene filled by different anorganic fillers

	Unfilled PP	20 % talc filled PP	20 % whiting filled PP	20 % lime filled PP
Falling weight impact at 20°C	10,0	8,3	10,2	10,8
Strength 10°C	9,0	4,8	8,5	10,8
-20°C	5,8	0,8	4,8	7,4
Tensile strength MN/m <sup>2</sup>				
at yield	5	4	5,6	7,0
at break	24	21,5	315	564
E modulus NM/m <sup>2</sup>	1,3	3,7	2,2	2,4
Flex. strength MN/m <sup>2</sup>	33,4	45,4	40,3	42,2
Heat dist. temp. °C	60	81	73	70

This additional cost means that a 50 % filled compound would be sold at a price per tonne comparable to or slightly lower than unfilled polymer, though with a specific gravity of 1,35 compared to 0,91. The improved stiffness however means that in applications where stiffness is important, wall thickness can be reduced, and in many cases a satisfactory finished product with the same weight as of unfilled polypropylene can be produced. This will usually result in a low raw material cost saving coupled with a substantial gain to processing costs, particularly for injection moulding, due to the more rapid cooling.

Where a lower filler content is desired, this can be most economically achieved by blending a highly filled compound with natural polymer, thus spreading the compounding cost. Due to the exceptional ease of melt processing of limestone filled polypropylene compounds even at high filler levels, the blending can be readily achieved.



Table 7: Comparison of calcium carbonate filled polypropylene with ABS

	50 % limestone filled PP	ABS (typical values medium impact grade)
Tensile strength MN/m <sup>2</sup>	23,0	48,0
Elongation at break %	5,2	10
Izod impact strength notched KJ/m	90	140
Flexural modulus GN/m <sup>2</sup>	3,37	2,7
Heat distortion temperature at 0,45 MN/m <sup>2</sup> at 1,81 MN/m <sup>2</sup>	112°C 66°C	98°C 95°C
Mould shrinkage %	0,8-1,4	0,4-1,9
Specific gravity	1,35	1,05

The real cost benefits occur however when the improvement in physical properties such as stiffness, or in processability, such as thermoforming, enables a filled polypropylene compound to be considered against another higher cost plastic material.

In many potential uses the low stiffness of polypropylene limits its applications despite its advantages, particularly economic benefits.

Improved stiffness can be traded against increased brittleness in the case of talc filled compounds, or increased cost in the case of fibrous reinforced polypropylene, or alternative materials such as ABS or rigid PVC. The improved stiffness of limestone filled compounds coupled with the retention of the essential toughness of polypropylene, enables them to compete with higher cost material such as ABS in many applications. This is demonstrated in Table 7 which plots the range of stiffness and impact strength achievable compared with other materials.

Apart from injection moulding, limestone filled polypropylene compounds are also suitable for profile extrusion, sheet and film extrusion and subsequent forming and blow moulding. An outstanding feature of these new compounds is their ease of processing despite the high filler content. A properly formulated 50 % limestone filled polypropylene compound for instance, can be injection moulded as easily as an unfilled material although a small increase in barrel temperature may be required. In common with most filled materials, there is a substantial increase in thermal conductivity compared with the virgin polypropylene. This leads to better heat transfer and hence more rapid cooling. Shrinkage is also reduced. These two effects lead to reduced cycle times on injection moulding and reductions in moulding defects such as sink marks.

Savings of up to 25 % on cycle times have been recorded where limestone filled polypropylene was used to replace high impact polysterene.

The improvement in melt strength of limestone filled polystyrene makes blow moulding and other melt forming processes much easier. Limestone filled polypropylene compounds with filler levels up to 40 % have been successfully blow moulded under identical machine and mould conditions to unfilled polypropylene. The increased cooling rate will normally lead to faster production speeds. The increased melt strength and range of limestone filled polypropylene together with faster heating rate make thermoforming of extruded sheet much easier than for unfilled polypropylene, normally considered a difficult material.

The major consumers of white carbonate fillers are the polymer (plastics and rubber), paint and paper industries. Calcium carbonate is regarded as the major bulk filler to plastics, i.e. it is the best product to reduce cost and crude oil consumption without significantly impairing strength. Where increased strength is required it can be used in conjunction with a reinforcing filler such as asbestos, mica and wollastonite (for plastics), or carbon black and precipitated silica for rubber.

Calcium carbonate is used as a filler throughout the range of polyvinylchloride and rubber products, polyethylene and polypropylene and other thermoplastics, although the particularly high quality end of the market in mouldings and extrusion has generally been served by the fine, uniform varieties of precipitated calcium carbonate rather than the natural product. This situation is changing somewhat as ultrafine carbonate natural carbonates are making inroads into the higher quality products.

The absence of statistics in the field of calcium carbonate fillers production and consumption makes any quantitative analysis of the market an extremely hazardous exercise. It is estimated, that Western European production of white carbonate filler /extender products is of the order of 4 mil. tons per year of which approximately 1.760.000 tpy chalk whiting, 2.200.000 white calcite and dolomite and 230.000 precipitated calcium carbonate.

#### Future development

There is a considerable potential for further development in the field of heavily filled plastics based on limestone fillers. Two particular areas are flame retardant grades, and the use of limestone fillers in polypropylene/ elastomer blends.

Limestone filled polypropylene compounds with high filler contents are inherently slow burning and nondripping. This improvement in burninh characteristics over polypropylene is alone sufficient for some applications. Probably will European automotive industry follow the US example by employing more and more plastic units in car manufacture especially kaolin and calcium carbonate filled.

Kaolin-hydrous, anhydrous and surface modified

Kaolin which is commonly called wlay or china clay is a hydrous alumino-silicate mineral. It is available in two primary grades:

the natural hydrous form and a calcined, anhydrous form.

The larger average particle sizes consists of mixtures of blocky and platy particles. The finer fractions are almost entirely thin plates.

The hydrous forms are non abrasive, chemical resisting, and have relatively high surface area, which promotes high viscosities. Their naturally acid pH must be considered in many systems wherein reactivity may occur. They disperse quite readily in most plastics, especially with the aid of dispersants or surfactants.

In reinforced or thermoset plastics, they control flow properties to provide more uniform composite properties.

Calcium kaolin is considerably harder, but provides improved electrical properties in thermosets and thermoplastics.

Many surface-treated types of each grade are available to provide outstanding water resistance, electrical properties, and reinforcement, in a variety of systems.

Kaolin is a common term for the mineral kaolinite, one of number of minerals called clays. Clay is a rock term applying to soft, earthy ores which are plastics when mixed with water. Large deposits are in the Piedmont Plateau area of Georgia, South Carolina and Texas, in Cornwall (Great Britain), Czechoslovakia, Germany, USSR, India, South and North Korea, Australia and many other places. The ores are generally associated with quartz, mica, carbon, iron and titanium compounds and sometimes a wide variety of other clay minerals, such illite, halloysite and montmorillonite. Open pit mining is usually employed.

Air floated grades are produced from dried ores which are passed through roller mills with internal air classifiers to remove coarse impurities and to disintegrate the ore to its natural state of subdivision.

Water leached grades are processed as water suspensions, in some cases treated by decolorizing agents or by high gradient magnetic separation, and fractionated with hydrocyclons or centrifuges to obtain specific particle size distributions, after which they are dewatered by vacuum filters or filterpresses. The coarser grades are obtained by drying the filter cake, whereas the finer grades are obtained by next separation. In either case, the dried products are milled to reduce agglomeration for plastic uses.

The water leached grades are generally used as the base kaolin to be calcined at lower temperatures for superior electrical properties or at higher temperatures for exceptional whiteness. Both are milled and air classified to reduce the hard agglomerates which form on calcining.

All of the above grades are treated with surface-modifying agents to obtain improved dispersibility, electrical properties, water resistance, and reinforcement in plastic systems.

#### Commercial products and properties

The single crystal of kaolinite is two layer hydrous aluminosilicate, consisting of chemically bonded layers of silica and hydrous alumina, and the form of hexagonal platelet. In the process of formation, some crystals were bonded together quite strongly to give rise to a range of natural sizes. Particles larger than about  $10\mu\text{m}$  (equivalent spherical diameter) are stacks of platelets with heights about equal to their average diameters. Those which are finer have different aspect ratios according to their size and the methods of disintegration. Below about  $2\mu\text{m}$ , all particles are thin platelets with average platelet diameters of 4-10 times the thickness.

Because the two sides of the kaolin particle are different and broken bonds at edges are highly active, kaolin exhibits a strong tendency to resist dispersion, by forming strongly bonded agglomerates. This is more pronounced with decreasing particle size. The active surfaces are, however, reactive with organo-silanes, various metallic salts such as vinyl stabilizers, polar polymers, lubricants and the like, to obtain a fairly complete state of dispersion. Surface treatment of hydrous or calcined kaolin is preferred to obtain the physical advantages along with improved bonding with polymers, ease of dispersion, better flow and non-reactivity in critical applications.



The naturally acid pH of the mineral causes undesirable reaction with epoxies and vinyls, unless the acid sites are inhibited by surface treatments; many such products are available for specific applications.

Both natural and calcined kaolin are more resistant to acids and alkalis than all but the more resistant polymers. Removal of the water of the constitution requires temperatures in excess of 750°C, much higher than plastics processing temperatures.

Table 8: Electrical properties of selected fillers

Mineral filler	volume resistivity ohm-cm		dielectric strength volts/mil	dielectric loss
	dry	humid		
kaolin, water leached	$10^{13}$	$10^{16}$	70 - 120	0,10
kaolin calcined	$10^{13}$	$10^8$	60 - 100	0,06
kaolin calcined hydrofobized	$10^{13}$	$10^{12}$	80 - 150	0,003
talc	$10^{14}$	$10^9$	200 - 400	0,001
mica	$10^{17}$	$10^{10}$	50 - 60	0,10

### Applications

Kaolin is principally used in reinforced plastics, where its platiness and its viscosity increasing effect prevents fiber "blooming" or the appearance of fibers as the model surface. Grades for this use should have very low 144  $\mu$ m (1325 mesh) contents since larger particle filter on fiberglass mats and cause a non-uniform distribution of filler, crazing, and poor physical properties.

Calcined kaolin also is used in electrical laminates to improve volume resistivity, and to reduce the concentration of titanium dioxide, due to the whiteness imparted.

In this and other applications, composite properties are generally influenced by the degree of dispersion of the filler and its packing. Because dispersion is so important to obtaining maximum filler effectiveness, surface treated grades are becoming more generally used.

The finer grades of kaolin are particularly effective for increasing tensile strength and modulus of low  $T_g$  thermoplastics, especially surface treated types, without attendant severe loss of elongation and impact strength.

Vinyl wire insulation is substantially improved by calcined kaolin at up to 30 phr. Hydrophobic surface treatment further improves electrical properties under wet or humid-aged conditions.

The use of kaolin is expected to follow the trend of greater filler use due to the increasing cost of polymers.

Many surface treated products have been developed in the past and it is expected that producers will utilize prior technology and further refine these products to offer a wider variety of more versatile kaolin fillers.

The polymer industry is an expanding outlet for china clay which is only one of a large range of minerals which can be used as fillers.

Fortunately, the scientific knowledge and experience we have gained carry out the extensive research and development work necessary to introduce china clay into a wide range of applications in the polymer industry.

Kaolin occupies an important position in the list of non-black fillers used in the rubber industry, and together with calcium carbonate are the most widely used of such materials. The reason for this is quite simple: clays can have the combined advantages of having reinforcing properties in rubber compounds together with relatively low cost. The range of available clays is wide, ensuring a variable performance/cost balance.

The many available types of clay are broadly classified into three groups. Two of these groups are based largely on particle size/shape differences and the third on a modified clay. The first two groups are often referred to as hard or soft clays, in American terminology. There is no clear definition of these terms, but it is generally understood that a clay will promote a higher level of hard physical properties and stiffness than will a soft clay. The hard clays have normally a higher index of plasticity and modulus of rupture.

Particles of kaolin or china clay as seen by the electron microscope are essentially hexagonal plate-like crystals, and it is the dimensions of these particles which largely control the effects of a kaolin in a rubber or plastic compound. Hard clays have a greater proportion of finer particles than do soft clays and the aspect ratio (Length: diameter ratio) of hard clays is usually higher. It is difficult to discuss average particle size, as particle size distribution can be quite wide. For complete particle size characterization a full distribution graph is necessary. This however is not always readily available and a useful indication of particle size effectiveness is given by a knowledge of the percentage finer than 2 microns and the percentage greater than 10 microns. Most kaolin used as fillers in rubber and plastic industry fall between the following limits:

	% finer than 2 $\mu$ m	% greater than 10 $\mu$ m
hard clays	75 - 95	0 - 5
soft clays	20 - 60	10 - 25

It is obvious that these two groups could contain clays of widely differing properties.

The third group of kaolins is commonly referred to as calcined clays. China clay consists essentially of the mineral kaolinite as referred above. Molecular water can be eliminated at high temperatures. This reaction is time and temperature dependent, but for practical purposes, temperatures in excess of 600°C result in the evolution of molecular water conversion of the aluminium silicate to an X-ray amorphous form known as meta kaolinite.

At temperatures over  $1. 100^{\circ}\text{C}$  new crystal phases appear, but it is in the X-ray amorphous region that products of interest to the rubber and plastic industry are formed. The most important properties of these materials are that they combine a high level of electrical properties, together with long term stability of such properties under adverse environmental conditions.

Hard or better, reinforcing clays are used where physical properties need to be of quite a high order and particularly where higher modulus or stiffness is required, in the vulcanized or unvulcanized compound. Common uses are in the footwear, high quality extrusions and some cables (mainly high voltage ones). Soft type kaolins are used where the level of physical properties is not so critical and advantage can be taken of the material suitability for use at higher loadings than hard kaolins to achieve a given level of stiffness and hardness. Applications include extrusion compounds and general mechanical mouldings. Both hard and soft types of kaolin are used when rubber and plastic products need to be acid resistant (e.g. for chemical plant lining). Soft kaolins are also used in some latex applications for example latex foam moulding, carpet underlays and carpet backing compounds.

The largest outlet for calcined kaolins is in the cable industry, particularly in medium and high voltage insulation compounds where synthetic rubbers are often used.

Most applications of kaolins are in growth where there is likely to be an increasing demand for existing materials (e.g. automobile components, industrial products, cables, building applications).

In one application (footwear) there is doubt about this growth due to the present increasing use of PVC in place of rubber in many types of footwear.

As processing and manufacturing equipment becomes more complex, and labour costs continue to increase, raw material costs will become relatively less important than consistency of quality and reproducibility of properties. This could lead to a decline in demand for indigenous materials as the requirement for internationally available products increases.

Interest in new products has largely centred around surface treated materials. This interest is likely to be maintained but must be supported by adequate technical data. The engineering thermoplastics have shown an impressive growth record in recent years. This record is due to research and development activities oriented toward improving the cost/performance relationship through filling the polymer matrix with surface-modified particulate materials. The surface modified kaolins improve the physical and chemical properties of nylons and reduce the cost of the composite. These kaolins, because of improved compatibility, permit highly filled polypropylene fibres and films. Recent reports indicate a cost /performance advantage of surface-modified kaolins in polyurethanes.

Laboratory data show potential advantages of the surface-modified kaolins in other systems as well. Considering the improved properties as well as potential cost reductions and crude oil lowering consumption, the surface modified kaolins are filling an industry need and creating a new series of filled polymers.

The trend, at least for the plastic industry, is to use surface modified kaolins. These are kaolins whose surface has been changed from hydrophile to hydrophobic and/or organophilic. The surface changes are accomplished by complete or partial coverage of the kaolin surface with organofunctional molecules.

The organic molecules can be attached by kaolin particles in different ways, namely:

- a/ chemical bonding
- b/ chemisorption
- c/ coating

The strongest attachments are formed by chemically reacting the organic molecules with the kaolin at the edges and surfaces. The strong covalent bonds thus formed are of the type produced by the reaction of a silanol with a chlorisilane. Chemisorption of the organic molecule to the kaolin particle is accomplished through weaker bonds of the hydrogen bonding or Van der Waals type. Although weaker, there is an integral unit formed by the organic molecule and the kaolin which is



not destroyed in high-shear compounding. The coating method shows little or no bonding and the coating can be readily removed by solvents or in compounding. Kaolin products produced by coating method are of very little interest to the plastic and rubber industries since all the normal processing techniques deal with either potential solvents for the coating or relatively high shear compounding, both of which will remove the coating from the kaolin.

The first reference to an organic derivative of kaolinite, the major constituent of kaolin clay, was made by Vivaldi and Hendricks in 1952. They prepared the methoxy derivative by the action of diazomethane on kaolinite.

Since that time, and especially in the past ten years, more surface modified kaolins have been described. The first commercial product, an organo-silicon derivation was introduced by Freeport Kaolin in the early 1960 s. Now there are many commercial organo-kaolin products on the market and more coming from the laboratories. The present surface-modified kaolin products are based on organo-silicon or organo-titanium reactants.

Obviously, surface modifications increase the cost of a filler or pigment and, unfortunately, kaolin is no exception. Therefore, the benefits that one realizes from the

use of the surface-modified filler must outweigh the added cost. As an example, consider the following problem:

"Produce a 3 to 5 denier polypropylene fiber containing at least 20 weight percent filler. Traditionally, fillers were used in fibres mainly as delusterants and only at levels of one percent or less. When the filler level exceeded about four percent, the fiber properties deteriorated to the point where the fiber was worthless.

Confirming the above, the conventional, fine particle kaolin was compounded into a fiber grade polypropylene at 20 weight percent. The compound could be melt spun into a undrawn fiber using extreme care. The hydrophilic kaolin surface was not wet by the organophilic polypropylene. Note that the kaolin particles are surrounded by voids. The resultant fiber could not be drawn since the fiber tenacity had been destroyed by the high filler level as the "state of the art" had predicted.

The kaolin used in the fiber was hydrophilic and did not work. Therefore, the surface of the same type kaolin was modified with the reaction product of tetraisopropyl titanate and oleic acid. The kaolin surface was the organophilic, especially so in hydrocarbon systems.

The same experiment, as described above - 20 % filler in polypropylene fiber-was performed with totally different results. The fiber lost none of its properties. The polypropylene wets the kaolin surface, and could be drawn to the fine deniers required.

Kaolins are not always treated to make them organophilic. Sometimes, the kaolins are treated to give a hydrophobic surface which has very little organophilic character. The wire and cable industry uses hydrophobic kaolins in filled ethylene-propylene (EP) elastomers at a 90-125 phr level.

For the wire and cable industry, calcined kaolins are surface-modified with organo-silicon compounds containing vinyl functionality. The surface modification enhances both the electrical properties and the physical properties. Again, comparing an unmodified kaolin in the same formulation one finds that the modified kaolin gave an insulation with a 55 % higher tensile strength than the insulation without the modified kaolin. The same compounds, when evaluated for retention of electrical properties in water, showed, that the insulation containing the surface modified kaolin was far superior.

The hydrophobic-organophilic character of the surface modified kaolins has created a new family of engineering plastics in the mineral filled nylon.

Table 9: 40 % Mineral filled polyamide (Nylon 66)

	unfilled	filled
Tensile strength, psi	11.900	14.000
Tensile elongation, %	60	8
Tensile modulus, psi	420.000	900.000
Flexural strength, psi	14.000	23.000
Deflection temperature 264 psi, °C	77	204
H <sub>2</sub> O absorption, % in 24 hrs	1,5	0,5

In 1970 it was shown that nylon 6, when filled with 38 percent by weight of an organo-titanium modified kaolin, had a heat distortion temperature 45°C higher than the unfilled control. The tensile strength because of the high degree of compatibility of the kaolin in the nylon, showed only a 6 percent drop despite the high loading. Since the original organo-titanium studies a surface modified kaolin has been designed which has as part of the organofunctionality, a pendent amine group. The presence of the amine makes the surface-modified kaolin even more acceptable to the polyamides. The general properties as such nylons, containing 40 % percent by weight of the amino-surface modified kaolin, are shown in Table 9.

The high deflection temperature permits the mineral filled nylons to be considered in applications which previously could only be made from thermoset systems. The significant reduction in water absorption in the filled nylon should result in an improved dimensional stability in parts subjected to severe changes in relative humidity. The strength properties, as indicated, have increased in a manner expected for fine particle filled systems. Presently, the mineral filled nylons are being used for several under-the-hood automotive applications, such as carburetor bodies, fan blades and others. Also as fender extensions and, interestingly, skateboards.

The compatibility of the amine, surface-modified kaolins in polyamides suggest that other nitrogen-containing polymer systems, such as esteramides, imides and urethanes, might also be compatible with the same modified kaolin filler. Field reports, from sampling of the amine, surface modified kaolin, indicate a high degree of compatibility with cast urethanes with significant property improvements.

The organo, surface-modified kaolins are presently being used in electrical insulation, nylon, selected rubber products, polypropylene fiber, white-opaque polypropylene film and other products. The modified kaolins are needed in this systems since conventional, nonmodified fillers will not do the job.

The higher cost of the kaolin is justified either in product performance or, in the case of high-priced polymers, as a cost reduction.

Demand for currently available material is likely to increase with emphasis on quality and consistency leading to a greater demand for finer and more reinforcing clays.

Use of calcined and surface-modified kaolin will increase as the demand for high voltage insulation increases. Apart from uses where good electrical properties are required, advantage may well be taken of other properties of calcined clays particularly where low water absorption and low permanent set are required. Most calcined clays are produced in the 50 - 60 percent below 2 $\mu$ m particle size range and are similar in reinforcing properties to a good quality soft kaolin. It is possible that finer materials than this may be required if large scale applications are to be found outside the cable industry.

### New products

New materials can be regarded in three groups:

1. Modifications to particle size or shape of existing fillers.
2. Surface modifications of existing materials e.g. surface treatment or coating.
3. Special purpose products to meet a particular need.

Plastic industry - the total amount of particulate filler used by the plastic industry is less than 10 percent by weight of the polymer used by the industry. Most of the filler is used in plasticized PVC polymer or copolymer to produce extruded sections including cables and floor coverings.

In the past, some plastic products and particularly some filled plastics products were made which were completely unsuited for the intended application. Today, fillers are used specially to enhance selected properties without too much deterioration of other properties and overall cost must be considered a property.

I believe that this will continue and will be assisted by the production of special fillers, the production of fillers modified by surface treatment, or the use of fillers in combination with other additives. The whole compound will be designed to be most "cost effective" method to meeting a particular set of requirements.

Polyvinylchloride cable compounds will become more heavily filled predominantly with natural or stearate coated whiting or specially prepared calcium carbonate and where necessary, calcined and hydrophobized kaolins will be used to re-establish the degree of electrical resistivity required.

Selected kaolins of certain mineralogical composition and particle size distribution can have reinforcing effects when used with limestone and plasticized polyvinyl chloride/acetate copolymer in floor tile compounds and can effectively replace asbestos in this type of composition.

Processing characteristics are unchanged and physical properties are up to the standard required by national and international specifications for vinyl-asbestos floor tiles. Additionally, the clay composition has superior color, better appearance and, lower water absorption and raw material costs may be lower. Also the handling difficulties associated with the finer grades of asbestos are eliminated.

The future looks good for surface modified kaolins and other pigments or fillers. Polymers such as urethanes, epoxides, imides, fluorocarbons, polysulfones and other newer materials are prime candidates for mineral filling.



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