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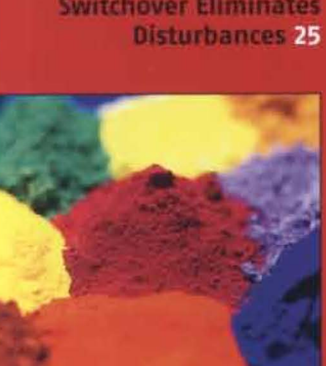

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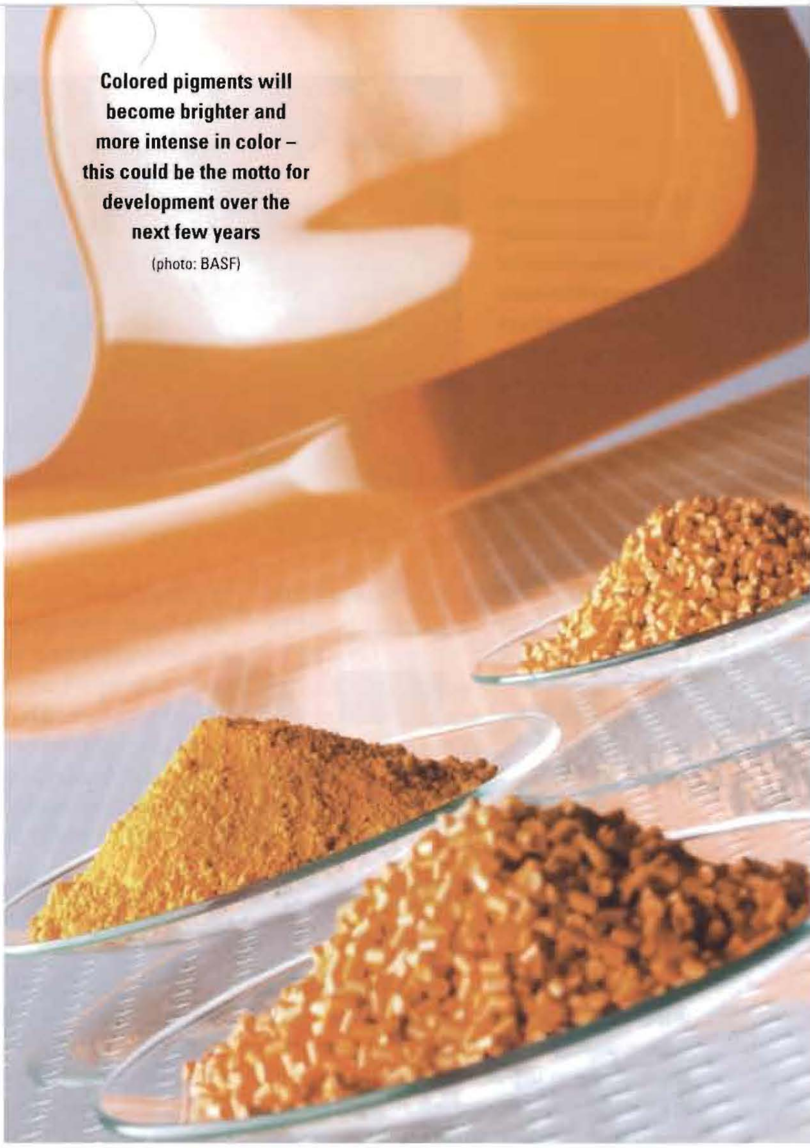
Color Diversity



Colored pigments will become brighter and more intense in color – this could be the motto for development over the next few years (photo: BASF)

Pigments. Product innovations in the area of pigments are mainly concentrated on colored, effect, and specialty pigments. The focus is on more intense shades and effects, because color designers are always looking for innovations to get away from the familiar. Pigments play a particularly important role in the consumer sector, where colors additionally serve as an inducement for continual new purchases.

WERNER RUDOLF CRAMER

Trend predictions are generally wrong and of little use as a rule. This also applies to color predictions: the automotive industry takes its cue from the fashion industry, the furniture industry looks at the automotive industry and the fashion industry searches for that elusive "zeitgeist". In short, each thinks it has found the ultimate wisdom and propagates its color vision. But in all of this, what always gets forgotten is that the applications being compared are completely different: automotive paints, fabrics, and plastics receive their color from different substances. For example, textile dyes cannot necessarily be used to color plastics, while effect pigments are just as unsuitable for dyeing fabrics.

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Leaving this aside, colors can only be produced if the right pigments are available. Heavy-metal-containing components are not used for pigment production, which already imposes a limitation. Unlike automotive paints, colorants used in the plastics industry have to cater for many different types of plastic, which react to pigments in different ways. For example, migration behavior and heat resistance are factors that can play an important role.

Color – a Sensory Perception

Let us return to trend predictions and cast an eye on the year 1856. Up to that point, the environment created by man was usually dreary, gray, dark brown – in fact, virtually colorless. Of course, churches were decorated with colorful paintings, while soldiers' uniforms, clergy vestments, and the garments of secular dignitaries had their special colors (even if the deep blue worn by the Prussian army was not exactly a bright color) but people's normal everyday world at that time was distinctly less colorful than today (**Fig. 1**). And although nature showed the way with its colorful blossoms and exotically colored animals, people were not able to imitate these examples themselves.

In 1856, William Henry Perkin, an English chemist, developed the first synthetic dye. This pale reddish-purple dye, called mauveine or mauve, was first used by a Scottish cloth manufacturer. Enthusiasm for the dye spread to England from France.

With his discovery, Perkin also really laid the foundations for the great colorant manufacturers ICI, BASF, Bayer and Hoechst. And you could even say that one double bond less in the pigments also turned these companies into pharmaceutical manufacturers. By today's standards, mauve was a very pale dye, which would not fire anyone with enthusiasm these →

Fig. 1. Many colors are produced from many different colored pigments. This is the only way to achieve the right shade (photo: Cramer)

Fig. 2. In the consumer sector, it is easy to play around with colors. Here color is used primarily as a purchasing inducement. Changing color combinations ensure that this inducement is continually refreshed (photo: Koziol)

days. But since that time, the successful advance of synthetic pigments has been unstoppable. The brilliant colors we enjoy today are the result of intensive research and gladden every designer's heart.

A second important step towards creating a colorful environment was the development of titanium dioxide pigment production on an industrial scale in the 1920s. Titanium dioxide occurs in nature as a black and white rock, which is usually stained with iron. Only after suitable chemical treatment does it become a snow white pigment that helps dark pigments attain their maximum chroma (intensity of color).

We often assume that all colors are available to the plastics industry. It should be remembered that in German the same word 'Farbe' is used to mean both the physical material with which color is imparted and the actual color sensation (e.g. red or green). In English and Dutch, a distinction is made between these two concepts with, for example, the words 'paint' (English) or 'verf' (Dutch) being used for the physical material and 'color' (English) or 'kleur' (Dutch) for the color sensation. (e.g. red or green). Color is a sensory perception that offers us an image of our environment. Without colors, there would be little or no means of making distinctions, i.e. to differentiate between ripe and unripe berries requires the ability to distinguish between red and green.

Colors are produced by pigments in the plastic that reflect some components of light and absorb others. The reflected components strike the retina of the human eye, providing a stimulus that travels via the optic nerve to the brain, where it is converted into color information.

Colored Pigments: Brilliant Colors

Colored pigments form part of the portfolio of large manufacturers. Sometimes – as is the case of BASF SE, Ludwigshafen, Germany, with Ciba – an acquisition is necessary to help complete the color portfolio and cover every color range. The original large pigment manufacturers had their specialties and concentrated on their particular color ranges (e.g. reds in the case of Hoechst). A similar evolutionary path to BASF SE was followed by Clariant AG in Muttenz, Switzerland, and today that company makes not only pigments but also masterbatches for plastics. Although they have the color range well covered, pigment manufacturers are always trying to gain market shares through new developments. Usually these developments are in the direction of higher color intensity to obtain more brilliant shades. This applies to all color ranges, particularly for violet and yellow to orange. The latter pigments can also be used for mixing in the green and red ranges **(Title picture)**.

Time and again, special new pigment developments breathe new life into the consumer sector. Color combinations are often offered, such as magenta, turquoise, and green or yellow, blue and red. Plastic parts with high brand loyalty change their color less frequently but instead a new shade produced with more intense pigments can be advantageous **(Fig. 2)**.

Effect Pigments: High Value

Another pigment range has also come strongly to the fore in recent years, again in the plastics sector. Interest in effect pigments has generally increased not just for automotive paints, packaging and cosmetics, but also in the plastics sector. The higher value of a plastics product is often one of the main reasons for preferring effect pigments over colored pigments.

As everyone knows, there are countless different grades of plastic. And each grade has its own mode of behavior with regard to pigments: typical examples include the

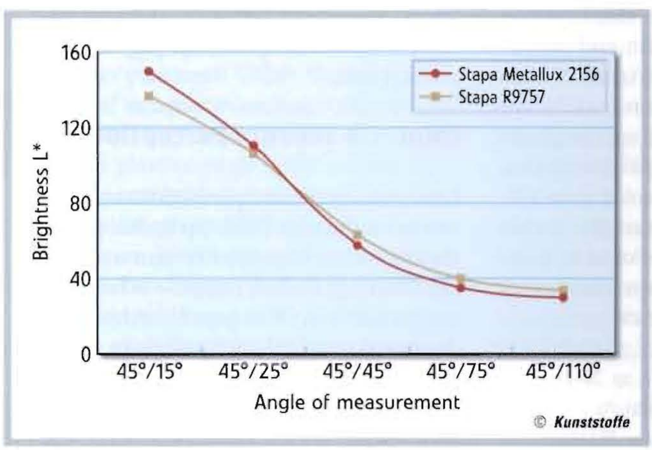

Fig. 3. The silver dollar (Metallux 2156) and cornflake (R9757) types of aluminum pigment have different brightness properties: the silver dollar is brighter close to the gloss angle but turns darker as the aspecular angle increases (source: Cramer)

cloudiness of effect paints in the automotive sector and the flowability of effect pigments in injection molding. Other problems are caused by, for example, ring lines or the extruder, through which effect pigments have to pass undamaged.

Effect pigments can change their color, depending on the viewpoint and illumination angle. A broad classification can be made between aluminum pigments, which reflect incident light, and so-called interference pigments. By these, we mean pigments which, on account of their structure, split the incident light into various parts and partly recombine it. In this process, light waves are superimposed on each other, which in physics is described as interference. Because of the different lengths of the optical paths, the resulting light wave is weakened or strengthened.

Fig. 4. Examples of plastics colored with aluminum pigments can be found in all applications, usually with higher-value products (photo: Schlenk)

Aluminum Pigments: Strong Lightness Shift

In nature, aluminum almost always occurs in chemically bound form and must be suitably processed. A basic distinction can be made between two types of aluminum pigment: through atomization of liquid aluminum, particles resembling potatoes are obtained. When rolled flat, these assume irregular forms, which in technical parlance are known as "cornflakes".

If the atomization is conducted under an argon inert gas atmosphere, tiny spheres are obtained, which when rolled flat give rise to disks. These disks are usually a regular shape and are therefore known as "silver dollars". With both types of pigment, there are different sizes and fractions, which are suitable for different applications in the plastics sector. "Silver dollars" are brighter and more brilliant than "cornflakes". These properties – and also the tendency to darken or lighten as the aspecular angle to the gloss angle increases – can be readily determined colorimetrically. The relevant geometries are specified in ASTM standard E 2194 "Practice for Multiangle Color Measurement of Metal Flake Pigmented Materials".

By adding other metals such as copper and zinc to aluminum, golden bronze pigments are obtained, which answer to mysterious names such as "Rich Gold", "Faded Gold" or "Rich Faded Gold".

Another method of producing aluminum pigments, besides atomization, is

Fig. 5. Fascinating effects can be produced with pearlescent pigments in all color ranges. In these objects, a white interference pigment is mixed with a colored pigment (photo: Merck)

deposition in a high vacuum. This method, known as physical vapor deposition (PVD), leads to the finest and most uniform particles. Companies such as Flex Products in Carlstadt, NJ, USA, use this method to produce effect pigments with strong color shifts. In this process, several layers of different metal oxides and aluminum are applied onto film. When the film has been comminuted and washed, the resulting pigments can in some cases change their color over three quadrants of the color space. This is due to laws of interference.

Eckart GmbH in Hartenstein, Germany, not only produces "cornflakes", such as Stapa Metallic R807, and "silver dollars", such as Stapa Metallux 2156, but also PVD pigments, which are marketed under the brand name "Metalure". Last year, Eckart took over production of Metalure pigments from manufacturer Avery Dennison Corp. in Pasadena, CA, USA, and integrated it into its US division **(Fig. 3)**.

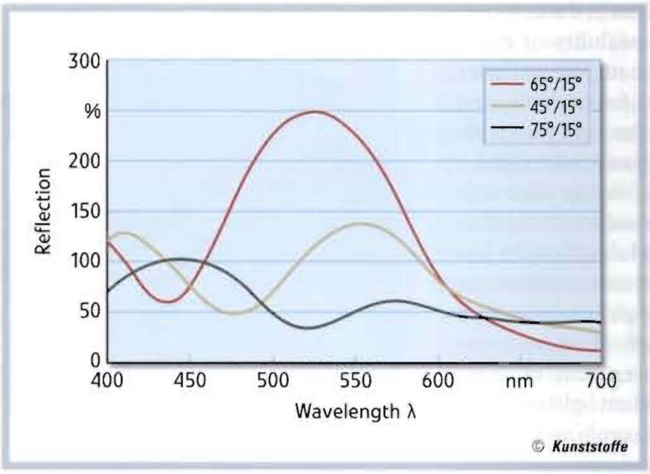

Fig. 6. Colored interference pigments such as CS Viola Fantasy display significant color shifts when the angle of incident light is altered. With the same aspecular angle, the maximum reflection shifts to short wavelengths with a flatter illumination angle (source: Cramer)

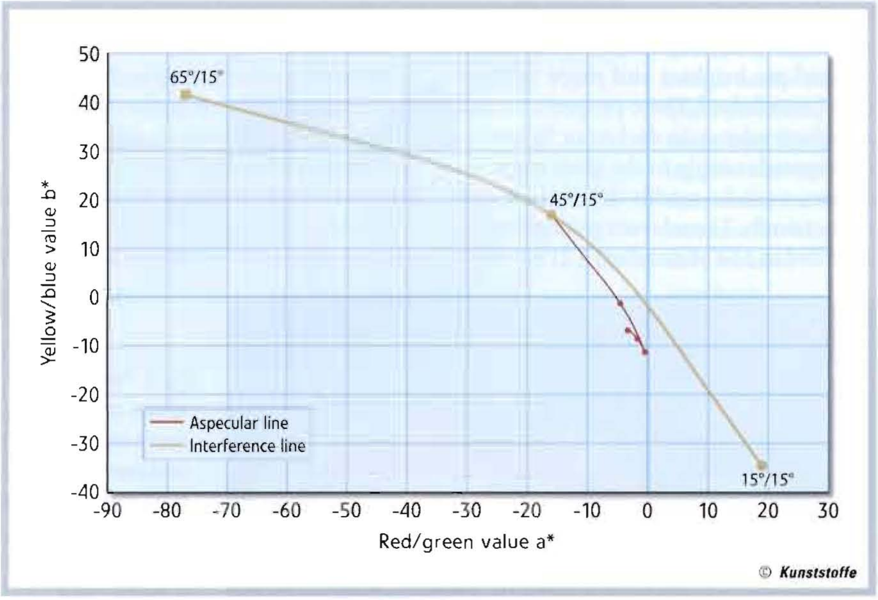

Fig. 7. The so-called interference lines and aspecular lines optimally describe an interference pigment. The interference line is based on measurements at different illumination angles and the aspecular lines on different aspecular angles with the same illumination angle (source: Cramer)

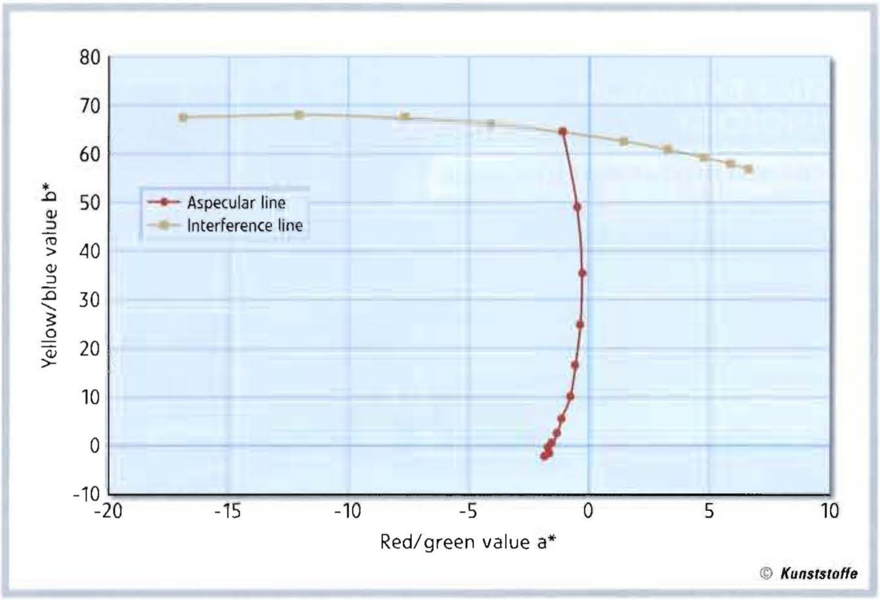

Fig. 8. Xirallic pigments have similar color intensity: for example, the color of Sunbeam Gold shifts from reddish to greenish yellow when the illumination angle is flatter (source: Cramer)

Schlenk Metallic Pigments GmbH in Roth, Germany, also supplies many different aluminum pigments for the plastics sector, either as pastes, pellets (e.g. Grandal P3100) or powder (e.g. Constant 3100) **(Fig. 4)**.

What innovations can be expected here in the future is difficult to predict. The trend is certainly towards more intense colors and effects. These can undoubtedly be achieved with existing aluminum pigments. On the other hand, color designers are always wanting innovations that, above all else, get away from the familiar, tried and tested solutions.

The use of aluminum pigments – and also of the interference pigments described as follows – certainly requires some experience to prevent pigment deformation or mechanical damage in, for example, the extruder. Nevertheless, interest in using these types of pigment in plastics is increasing and that applies not just to the low-cost sector but also to the higher-value consumer market.

Interference Pigments: Iridescent Effects

This group of effect pigments is one of the newer types, which, as described, derive their name from the physical phenomenon of "interference". This phenomenon is often found in nature in beetle shells, butterfly wings or snail shells. Since the light waves are refracted and reflected in different layers, fading is virtually excluded. One discovery in the Mes-

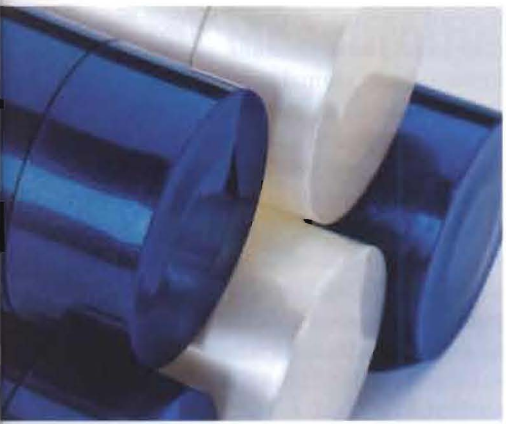

Fig. 9. Natural raw materials are not usually available regularly or in sufficient quantities. They may also contain impurities that make further processing difficult. The trend is therefore towards synthetic carriers for interference pigments (photo: Eckart)

sel pit fossil site near Darmstadt, Germany, shows a beetle in its full colorful splendor even after 47 million years.

Attempts to produce this iridescent effect artificially have been going on for a very long time. The Frenchman Jaquin produced so-called fish silver from fish scales for the first time in 1655. Traditionally, the effect has also been created using bismuth oxychoride, a substance with a natural pearlescent effect.

Modern interference pigments usually consist of a transparent carrier layer such as mica, aluminum oxide or silicon dioxide **(Fig. 5)**. Onto this carrier platelet, one or more highly refractive metal oxide layers are applied by a wet-chemical process. After drying, iridescent particles are obtained, which, when coated with titanium dioxide, give rise to silver white or pearlescent particles. With iron oxide, copper red interference pigments are produced and with the combination of both metal oxides golden yellow interference pigments. If the pigments are based on mica or aluminum oxide as the carrier material, the color shift is not so pronounced (e.g. from yellow-green to blue-green, when the angle of illumination is changed for the same aspecular angle. With silicon dioxide as the carrier material, this color shift is much greater, so that pigments like Colorstream Viola Fantasy change their color from green through yellow to violet **(Fig. 6)**.

Modern colorimeters determine the color change of these interference pigments and are used to characterize and identify them **(Fig. 7)**. The geometries – consisting of the illumination angle and viewing angle – are specified in US ASTM standard E2539 "Standard Practice for Multiangle Color Measurement of Interference Pigments". This standard is deliberately confined to pigments and can be used for all applications.

In addition to color, the phenomenon known as "living sparkle" is also of interest. Although it is not physically defined, it describes a phenomenon similar to "dancing" light reflections on a turbulent surface. Pigments of the Xirallic type on an aluminum oxide carrier display this sparkle effect. Interestingly, the effect increases with decreasing concentration of Xirallic. Once again, there is great interest in reproducing this effect in some kind of form, and describing and measuring it.

Previous solutions are based on photos taken of samples under different illumination angles. With the aid of digital image processing, evidence can be obtained about the strength of the sparkle. With this information, it is possible to make comparisons, for example, in the case of a new batch. A totally satisfactory solution has not yet been found; various institutions and manufacturers have collaborated on "red sparkle" to work further on this phenomenon. The US standards organization ASTM has also defined this phenomenon in a task group.

These interference pigments are produced by some well-known major man- →

ufacturers. The world's largest producer is Merck KgaA in Darmstadt. Its portfolio ranges from bismuth oxychloride pigments (BI-Flair) through traditional Iriodin pigments with natural mica as the carrier material and the above-mentioned Xirallic pigments, to Colorstream pigments with silicon dioxide as the carrier **(Fig. 8)**. Synthetic mica platelets are also used for the Miraval pigments group.

These pigments are also supplied in exterior grades with special additional stabilization for outdoor use. The pigments usually come in different particle sizes, offering a choice between a fine silky shine or stronger effect.

In acquiring Engelhard Corp. in Iselin, NJ, USA, BASF had the autocatalysts sector primarily in mind. The fact that Engelhard was also a major manufacturer of effect pigments played a less important role in the acquisition. BASF had previously decided to scale down its activities in the area of effect pigments (Variocrom, Paliocrom). The same happened with the acquisition of Ciba AG in Basle, Switzerland. Besides rounding out its portfolio of colored pigments, BASF was also able to expand its range of effect pigments through the addition of the interference pigments from Ciba. With its "Hi-Lite" pigments (formerly made by Engelhard), BASF now has a complete range of interference pigments. The company also supplies other pigments for use in the plastics sector, such as "Glacier Frost White" and the mica-based Lumina pigments.

In the interference pigments sector, it is very difficult to make predictions about future developments. Interference pigments are one-offs that cannot be adjusted by mixing with other pigments as in the colored pigments sector. Important pigments in, for example, the white range already exist, and the trend could continue in the direction of even whiter pigments if the pigments become more opaque at the same time **(Fig. 9)**. Interference white can be mixed with all color ranges, so there is a sufficient range available. Additional effects, such as sparkling, could certainly increase or trigger interest in interference pigments exhibiting this phenomenon.

Biopigments: Back to Nature

The history of pigments starts in nature. Right from earliest times, people have used anything suitable that nature had to offer for painting and dyeing. The purple Murex snail, which is so often mentioned, became a symbol for the color purple. Thousands had to be collected to obtain a small amount of dye. The cochineal scale insect yielded carmine, another well-known dye of animal origin.

These days, natural dyes are supplied by pigment manufacturers or, as in the case of interference pigments, natural micas are used as a base material. But the problem with natural resources lies in their uncertain availability and natural impurities. In addition, the present demand for pigments could definitely not be met with natural products.

Outlook

Pigments are an integral part of plastics. They make them look more appealing for the particular application. Besides so-called "house" colors, there are many design colors in the portfolios of pigment and masterbatch manufacturers. As a result, our world is becoming ever more colorful and colored objects define our environment. New colors also serve as a purchasing inducement. Their use in plastics is as diverse as plastics themselves. ■

THE AUTHOR

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High-Pressure RTM Installation for High Process Requirement

Pressing Technology. Short cycle times are essential for economic production of fiber-reinforced parts. That is why the high-pressure RTM process is growing increasingly important. Rucks Maschinenbau GmbH, Glauchau, Germany, has joined forces with a customer to develop the RKV 293, a high-pressure RTM installation. This is designed for very high press forces and high-precision parallel and displacement control.

The customized press must generate pressing forces of up to 25,000 kN, with the exact force depending on the mold and workpiece size. Non-uniform pressure distribution in the mold during resin injection is counteracted by several displacement-controlled hydraulic cylinders. Thus, even in the case of eccentric loading, parallelism of the mold halves of ± 0.05 mm/m is guaranteed. Displacement accuracy of the pressure plate of 0.05 mm and a deflection of less than 0.1 mm/m also ensure high product quality. Some applications additionally require tangential deviation of the pressure plate. Through the four displacement-controlled pressure cylinders, a tangential deviation of ± 0.2 mm can be achieved in such cases.

The economics are further boosted by means of an integrated double-sided sliding table with movable mold carrying plate. This solution allows the customer to load a second mold during the pressing process and makes for rapid tool change. Furthermore, ergonomic mold loading and component removal are ensured.

The integration of the RTM installation into the press controller and the dedicated RTM process software (type: Ruxx-Logic, same manufacturer) makes for high process reliability and intuitive operation. Quality control and assurance are provided by Rudas data acquisition software, which logs all parameters during the pressing process and makes them available for further processing.

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