Introduction

The last decade is characterised by a profound evolution in radiation curing (RC) technologies. For this reason, it has become a widely used technique in numerous industrial processes such as wood-finishing, metal coating and the embedding of electronic materials. Additionally, radiation curing gained success in the field of silicone release coating-manufacturing and is nowadays well established and rapidly growing. In the following text we aim to summarise our developments in this field within Goldschmidt.

Silicone Acrylates

Parallel to ongoing developments in the field of solventless silicone release systems Goldschmidt started its own activities and in 1983, radiation curable 100% solvent-free silicone acrylates were introduced into the market. Compared to other radiation curing silicone systems, silicone acrylate based products provide the opportunity to be cured by either ultraviolet light (UV) or electron beam (EB).

In the chemists view, these substances are liquid polydimethylsiloxane prepolymerms. Radiation curable groups are introduced into the molecule via modification with acrylic acid. Reactivity and degree of crosslinking are adjustable over a wide range by varying the functionality (i.e. concentration of reactive groups) and constitution (i.e. steric arrangements of reactive groups within the polymer chain). Due to the numerous possibilities of variations there results a large spectrum of products with different characteristics.
The cure is based on the polymerisation of the acrylic C=C double bond via a radical chain reaction. In the EB curing process a sufficient number of radicals for spontaneous polymerisation is produced due to the high radiation energy whereas with UV light the energy is not as intensive thus a photoinitiator is required for a UV process. The required high local radical concentration is provided by its decay.

**CHART 4**

The radical generation and immediate chain-growing leads to rapid and efficient crosslinking even at room temperature. It is for this reason that silicone acrylates cure immediately, i.e. in less than one second.

**Application**

For the production of radiation cured silicone release liners essentially the same equipment is needed as for thermally cured coatings; with the exception of the dryer, which is replaced by an EB- or UV-unit. Unwind, coating head, and rewind station can be identical. Since the radiation unit required takes up considerably less space than curing ovens, in a number of cases it is possible to insert such an unit into an existing conventional production line without extensive changes.

**CHART 5**

However, since TEGO RC Silicones are 100% solventless products, consideration must be given to the coating head. A good control of the coat weight is required for obvious cost considerations. Pinhole free films must be applied to prevent migration of the adhesive to the substrate. All coaters capable of handling 100% thermally curing silicones are suitable for the use with Goldschmidt's RC Systems.

Most of our experience lays in the field of multi-roll smooth roll coaters. We find that this equipment will give excellent results at high production speeds. Even with coat weights of approximately 0.9-1.2 g/sqm on paper or 0.6 g/sqm on plastic films uniform pinhole-free silicone coatings can be reliably achieved. Extensive work is being done in the industry using other types of equipment; including: differential offset gravure, porous roll, and reversed roll coaters.

In contrast to other silicone release products, the thermal stability of TEGO RC Silicones offers the possibility of using a novel process technique. Coating at elevated temperatures up to 60°C leads to improved surface coverage due to reduced viscosity and better rheological properties of the warm silicones. Even formulations containing photoinitiators can be applied in this way without gelation on the equipment.

**Inerting**

A basic effect in the radical polymerisation is its inhibition in an air containing atmosphere. Molecular oxygen as a stable diradical is not able to initiate polymerisation, but readily reacts with other radicals. Therefore the growing radical chain is effectively terminated by contact with oxygen. Because of the large O₂ excess, the reaction of free radicals with oxygen is approx. $10^5$ times faster than with another acrylate molecule. The limited chain growth leads only to short, still liquid polymers and results in a wet or tacky substrate surface, which is unfit for further use.
These undesirable effects are eliminated by curing in an inerted atmosphere. The most efficient way is by the use of nitrogen blanketing. By flooding the reaction chamber with nitrogen the concentration of oxygen can be reduced to some ppm. Goldschmidt has done active research and development on the optimal constructional design for inerting radiation curing lines. We have worked out the significant parameters for effective and efficient inerting, which are summarised in our inerting concept. Due to this improved know-how in inerting technique the consumption of nitrogen can be drastically reduced while still obtaining the necessary low oxygen levels. The preconditions for effective inerting and minimum inert gas consumption include an effective barrier nozzle at the entry side, since the boundary layer of oxygen on the coated side of the substrate has to be completely replaced. This can be done effectively with an adjustable slit nozzle with laminar gas flow. The opening of the barrier nozzle should be maximum three times the distance between nozzle and web and the angle between web plane and nozzle should be in the range of 3-10°.

In order to guarantee rapid safe purging, the reaction chamber should be designed to have a volume as small as possible and a simple geometrical shape. To ensure that nitrogen loss through leakage is kept to a minimum, careful sealing of the chamber and on the exit sides is recommended. It is also useful to add a blade, to guide the rolls at the entry and exit sides. The ideal way to uniform nitrogen distribution in the chamber is done by means of a perforated manifold tube. Purging should take place against the web direction. Accurate monitoring of the oxygen level at multiple points is another important factor to guarantee accurate inerting.

In case you have further questions, we have a brochure with more detailed information on this subject and, of course, we are also prepared to give practical assistance to those, who want to install a new line or retrofit their existing one.

In our mobile UV units, theory was turned into practise. Their inerting technology were tailor-made for the requirements of TEGO RC Products.

Pilot Plants

To work out the properties of radiation curing silicone acrylates, we installed in cooperation with Pagendarm and RPC a pilot electron beam unit located at Pagendarm's technical center in Hamburg, Germany with a working width of 1.25 m (49 inch) and line speeds up to 600 m/min (2000 ft/min). It is running since mid of 1991.

For the practical demonstration of UV-curing, in summer 1992 we introduced a mobile UV facility with a working width of max. 1.60 m (63 inch) and two 100 W/cm medium pressure Mercury UV-lamps from Eltosch. The base plate was manufactured by GTU (Hamburg/Germany). The mobile UV-unit can be integrated into existing solvent-free siliconising lines for industrial testing. Up to now this mobile UV-unit has proven its usefulness, since numerous successful trials with different customers all over Europe were made and the waiting list for interested parties is growing. Apart from customer trials we also installed the UV-unit at the Kroenert technicum in Hamburg/Germany for some time and used it for basic research on new development products.
In order to serve the needs of US-customers a second mobile UV-unit from Convertech (UK) was constructed with a working width of max. 1.07 m (42 inch), equipped with a 240 W/cm (600 W/inch) UV-lamp from Aetek (Illinois/USA).

Apart from that, it is also worth mentioning that due to the growing interest in radiation curing technology nowadays more and more equipment suppliers, e.g. Polytype (Switzerland), Kroenert (Germany), Prime (USA), Faustel (USA) and Fusion (USA, Europe, Japan) have the technical background to manufacture state of the art inerted UV machines.

Examples

Depending on a number of factors (e.g. adhesive, substrate, final product), there is a need of proper adjusting different release levels. TEGO RC Products offer the complete range from easy via controlled to supertight.

**CHART 9**

By mixing different components of our RC Products, release levels can be fine-tuned to meet the customer requirements. A typical example is shown in the following chart.

**CHART 10**

Some of our work has been focused on the question of the compatibility of RC Silicone Acrylate release coatings with common adhesives. Different types of adhesives with thermally cured release liners (solvent containing and solventless), provided by several well known European producers of self adhesive materials, were included in the study. The tested adhesives belong to the categories of rubber based systems and acrylic dispersions.

In order to compare the original laminates and the same adhesives on RC materials different substrates (glassine paper, clay coated paper and polypropylene film) were first coated with an easy release product and then cured by UV. The adhesives have been laminated onto these release liners and afterwards stored under defined conditions, together with the original materials. After certain periods, the release values are evaluated and compared to those of the original materials.

**CHART 11**

Some of our results from the group of acrylic dispersions are shown in chart 11. In this graph, the data blocks on the left side represent the values of the original laminates whereas the results for the RC Products are shown by the right rows. The release values are determined according to FINAT #3 (i.e. a constant stripping speed of 30 cm/min (12 inch/min) and an angle of 180°). Although the types of adhesives differ in their specific properties, it is clearly shown that there are no major differences between thermally and radiation cured silicone acrylates. RC Silicones meet the technological trends in the industry and fit into customer requirements.

Advantages of Radiation Curing

The radiation curing technology leads to a number of advantages, resulting from the absence of heat and the different curing mechanism.
Resulting from the absence of a catalyst, the danger of catalyst poisoning is not given. This may be of importance if you are looking at special paper qualities like e.g. recycling papers. Due to the complete curing, there is no postcuring after the product leaves the UV chamber or the electron beam zone. Therefore, release values are immediately stable, so that in-line processing such as siliconising, adhesive coating and laminating in one run is possible.

As a result of the ability to cure at room temperature, the use of a large palette of substrates, even heat sensitive ones, is possible. Additionally, no paper shrinking occurs and the remoisturing unit is no longer necessary. In cases of double sided coated papers, problems like blistering are also eliminated.

In the area of process engineering, there are also new opportunities. The compact construction of a radiation unit takes up considerably less space than curing ovens, and in a number of cases it is possible to insert such an unit into an existing conventional production line without extensive changes (this was successfully done at Pagendarm's technical center). In addition, high line speeds - without misting - and lower energy consumption are further economical benefits.

Conclusion

The concept of radiation curable siloxanes has proven to be extremely promising. Of course we will continue our work in upgrading, expanding and improving the Goldschmidt product range. Present market reactions and the intensive use of our pilot facilities indicate that we and our customers are already well on the right way to success.

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362 (Charts are omitted)