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Global Release Liner Industry Conference 2008

OPTIMISED TECHNOLOGIES ARE EMERGING WHICH REDUCE PLATINUM USAGE IN SILICONE CURING

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Global Release Liner Industry Conference 2008 was organised by AWA Alexander Watson Associates BV and took place from 6th to 8th February 2008, at the Hilton Amsterdam Hotel, The Netherlands (1). It was attended by all the major players in the silicones industry, major label and paper manufacturers and representatives of the precious metals industry. The conference focused much attention on the development of next-generation low platinum catalyst solutions and the potential for complete removal of platinum from silicone curing systems. This review describes the technical developments, their related benefits and shortcomings, and summarises the trends expected to prevail in the release liner industry during the next few years. The release liner industry is an important sector of the overall market for silicones.

Background

Silicones, or polyorganosiloxanes, are used in a variety of applications, particularly in pressure-sensitive adhesives and release coatings. A key market in this sector is that of release liner coatings for labels and tapes, where the good adhesion and clean release properties of silicone release coatings are highly desirable.

Platinum is widely used as a catalyst for the curing of these silicones by promoting a hydrosilylation reaction, Reaction (i), (2):

$$R_3SiH + H_2C{=}CHR' \xrightarrow{\text{Pt catalyst}} R_3SiCH_2CH_2R' \quad \text{(i)}$$

Karstedt's catalyst (chloroplatinic acid-*sym*-divinyltetramethyldisiloxane complex) is a Pt(0) complex containing vinyl-siloxane ligands, and it initiates the addition of a silicon–hydrogen bond across a carbon–carbon double bond, known as curing, which hardens the silicone by crosslinking siloxane chains, Figure 1. The reaction, at temperatures in the region of 80 to 120°C, is carried out in a platinum-containing Karstedt's catalyst bath in which the silicone is cured rapidly as the paper label, or 'labelstock', is applied to its backing, forming a release coating between the two layers on a sub-second timescale. Free radical-based alternatives to platinum catalysis, initiated either by ultraviolet (UV) light or an electron beam, can be used to generate the radical initiator, but require labile groups such as epoxides or acrylates and thus the properties of the cured silicone vary from conventional silicones.

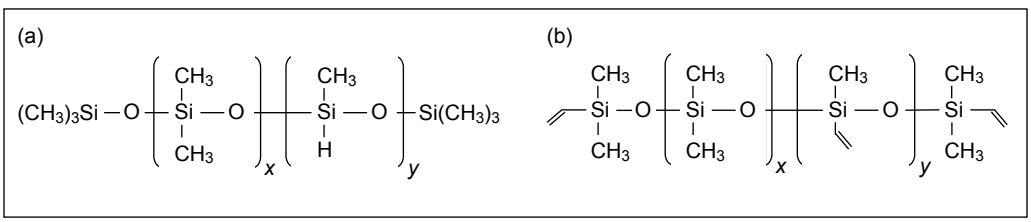

Fig. 1 (a) Silicone monomer typically used in solventless platinum-catalysed hydrosilylation reactions; (b) Conventional crosslinker for platinum-catalysed hydrosilylation reactions

Platinum in the Release Liner Industry

Presentations were given by silicones suppliers Dow Corning, Bluestar Silicones and Wacker Silicones, and perhaps the hottest topic of the conference was that of platinum, its price and ways to reduce its usage. Platinum-catalysed thermal curing remains the industry standard approach and because the catalyst is irretrievably lost in the product, the cost of platinum is one of the biggest challenges facing the industry today.

Highlights related to platinum included a joint presentation by Norm Kanar (Dow Corning, U.S.A.) and Wolfgang Wrzesniok-Rossbach (W. C. Heraeus, Germany) entitled 'Platinum Challenges: Trends and Developments', showcasing the cost benefits of Dow Corning's low platinum product series. There was also a paper by Karsten Schlichter (Bluestar Silicones, France), entitled 'Radiation Curing Silicone Release Systems, the Pt Alternative?', appraising a range of curing chemistries. According to this presentation, the market split between platinum and radiation cured systems is expected to stand at around 80:20 by 2015 compared to 85:15 at present. A small and diminishing share of the market uses solvent-based tin-catalysed emulsions, but this is expected to fall to zero within the next few years, according to these projections. Taking a slightly different angle, Hans Lautenschlager (Wacker Silicones, Germany) described smarter ways of monitoring and using silicone in his presentation 'More or Less Silicone?'.

Growth in the silicones industry is strongly linked to growth in consumer spending, as labelstock is primarily a consumer-driven industry. Annual global growth of around 5 per cent is expected for the next few years. In terms of platinum uptake, industry growth will be at least offset by the increased use of low platinum solutions, particularly when platinum prices are high. During this conference, platinum successively set then-record high prices, fixing in London at U.S.$1852 per troy ounce on 7th February and U.S.$1860 per troy ounce on 8th February (3).

Low Platinum Technologies

Johnson Matthey estimates that the silicones industry worldwide used around 180,000 troy ounces (5.6 tonnes) of platinum in 2007 (4), which at average Johnson Matthey base prices for the year of U.S.$1307 per troy ounce, is worth around U.S.$235 million; in the eighteen months from the start of 2007 to July 2008, the price of platinum almost doubled (3). This accelerated the development of low platinum technologies, which have the advantage of being largely drop-in replacement systems for existing coating units, unlike free radical initiated systems. Through advanced engineering of the silicone polymers and crosslinkers, Dow Corning has developed a system which allows the use of a catalyst bath containing only 25–35 ppm platinum, compared to the standard 100 ppm typically in use around the industry. Dow Corning claims that its "branched polymers [and] a new crosslinker structure… [which] enables cure of the release coating at platinum catalyst levels as low as 25 ppm" (5) can overcome operational and performance issues typically seen with the modified components in the radiation-cured field. Bluestar Silicones and other companies market similar solutions, which are commercially available. The feeling in the industry is that platinum reduction, rather than widespread uptake of UV solutions, is likely to be the key trend in the next decade. The technical barriers to reduced platinum usage are less significant, less costly and appear closer to being resolved.

The market share of platinum-based solventless emulsions remains at around 85% according to Bluestar Silicones, who themselves offer a platinum-free option to paper manufacturers. This level of market share is unlikely to decline significantly in the near future, although as explained below, platinum-free UV cured systems will continue to take some market share, most likely in lower performance applications.

Non-Platinum Technologies

Free radical-initiated curing was pioneered by Goldschmidt GmbH, latterly Degussa and now Evonik, in the early 1980s and has gradually taken limited market share since that time. The technol-

ogy uses unconventional side chains such as epoxy and acrylate groups to generate free radicals at ambient temperature, usually by UV activation, as shown in Figure 2, (6). Occasionally cationic curing can be used, although only under certain process and substrate conditions. Evonik state that 'post-curing' in both UV-initiated and in particular cationic systems can be a problem (7), in other words the rate of curing is not comparable to the platinum-catalysed reaction. The UV process itself displays operational and product performance limitations, in terms of clean release and rate of curing, which has a direct impact on the throughput of the coating equipment. It is generally thought that both coat weights and curing times are higher for radiation-cured silicones, although a number of companies claim to have achieved similar curing times and therefore throughput to the conventional process. This would represent a significant technical advance, and may promote the transition to non-platinum technologies in the future.

In a paper entitled 'The Influence of the Release Liner on Label Properties', Hervé Vigny (Label Experts, France) described a phenomenon known as the 'zippy effect', observed in UV-initiated systems. After curing, the adhesion of the label to the release liner takes some time to stabilise, compromising the clean release performance of the product. Although the effect is not fully understood at this time, the cause is widely thought to be the modified side chains which are essential for UV-initiated processes.

Perhaps the greatest barrier to a move to UV technologies is the significant capital and operational expenditure needed to install the UV light source and its related equipment. There are also process control issues associated with the requirement to carry out the reaction in an inert atmosphere of nitrogen. Opinion varies on whether the transition is financially viable at all, even at the platinum prices that were current at the time of the conference. In an industry relatively averse to change, conventional methodology is not expected to be displaced quickly.

Conclusions

Global Release Liner Industry Conference 2008 focused on the key topic of platinum usage in silicone curing applications and potential opportunities for reducing the amount of platinum used. These include the use of advanced silicone monomers and crosslinkers to reduce the amount of platinum catalyst required, or the use of alternative curing technologies, specifically UV-initiated free radical curing. Low platinum solutions are becoming available to the release liner industry from silicones manufacturers and are expected to achieve significant market share within a few years, as high platinum prices (at the time of this conference) stimulate efforts to use less of the precious metal. Doubts over the financial viability of installing and using radiation curing technology remain, as do technical limitations of the product and process, meaning that this production method will only be used for around twenty per cent of release liner curing applications in the next decade, with the balance still to use platinum catalysts.

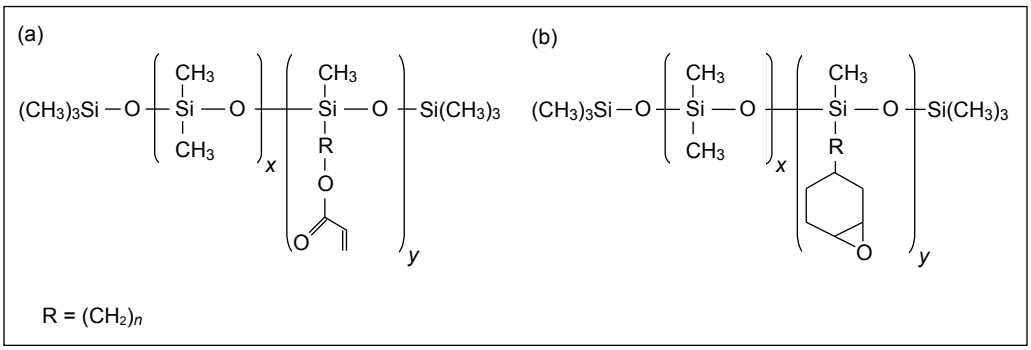

Fig. 2 (a) Acrylate-based crosslinked silicone, as produced by UV-cured process; (b) Epoxy-based crosslinked silicone, as produced by UV-cured process (6)

Acknowledgements

Publically available literature from Dow Corning (8), Bluestar Silicones (9), Wacker Silicones (10) and Evonik (11) was used as background information for this review. Global Release Liner Industry Conference 2008 was organised by AWA Alexander Watson Associates BV.

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The Reviewer

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