Cationic UV Curable Silicone Release Coatings: A Historical Perspective and New Formulation Tools

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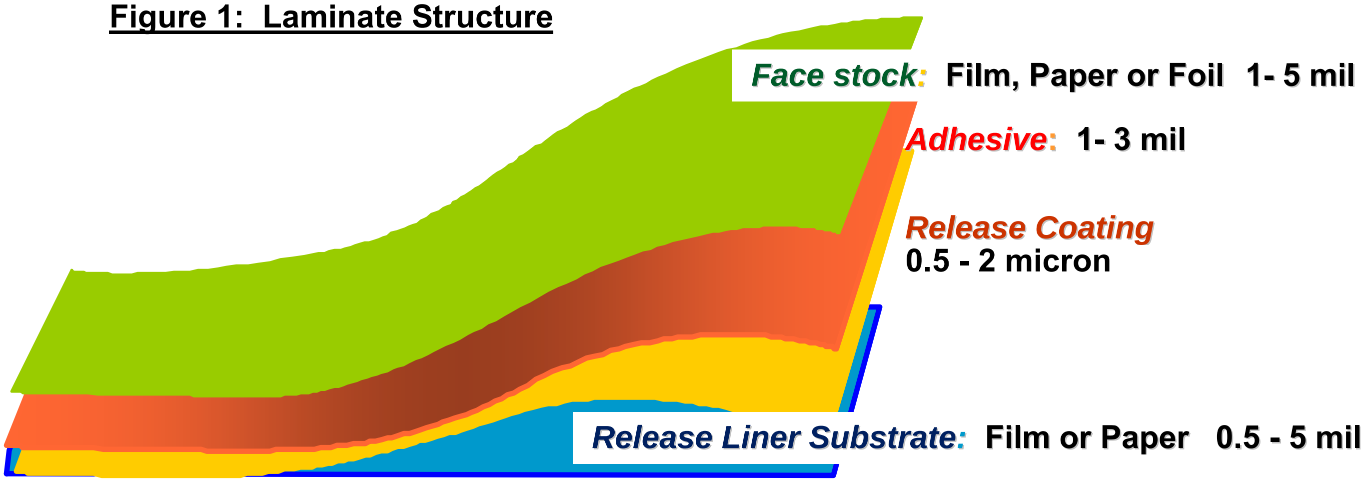
Abstract

Cationic photocurable silicone release coating systems based on cycloaliphatic epoxy functional polydimethylsiloxanes and 'onium salt photocatalysts are established commercial materials. The incompatibility of polar photocatalysts and other additives with silicone media plus the need to balance release performance versus efficient UV cure have driven design of these coating systems. New Iodonium phosphate catalysts and sensitizers with good silicone miscibility plus excellent photo-response have been shown to effectively promote cationic UV cure of silicone coatings.

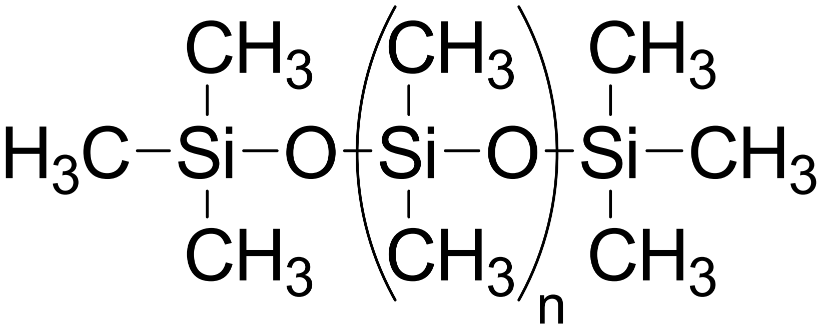
Background: What is a release coating?

Pressure-sensitive adhesive labels, postage stamps, and other such articles are familiar items of commerce. These items usually require a *release liner* to be bonded to the adhesive coated backside of the label. Solid, crosslinked polydimethylsiloxane (PDMS) was found to be a good release surface some 60 years ago[1]; this discovery gave birth to the modern pressure sensitive (PS) industry. A typical 2 ply pressure sensitive label construction is illustrated below.

Figure 1: Laminate Structure



A PS laminate such as shown above might be ~ 6 mil thick, of which the silicone release coating makes up less than 1% of the width. Paradoxically, the release coating has to both 'lightly stick' to the PSA *and* easily release from it in order for the label construction to function properly. Failure of the very thin silicone coating to predictably detach from the PSA renders the label unusable. Many organic and inorganic substances including waxes and certain alkyl carboxyl complexes of chromium, for example, can release tacky substances, but polydimethylsiloxane surfaces provide the most consistent and controllable release of pressure sensitive adhesives. The PDMS structure responsible for release performance is depicted in Figure 2.



$$H_3C-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{Si}}}}-O-\left(\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{Si}}}}-O\right)_n-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{Si}}}}-CH_3$$

Figure 2: Structure of Polydimethylsiloxane. Typically n > 50.

The chemistry and physical structure of linear PDMS results in hydrophobicity, low reactivity, low surface energy, and *very low* Tg. Departure from the basic PDMS structure compromises release performance to some extent.

As the PS industry evolved, silicone suppliers developed thermally curable silicone release coatings that could be easily applied to dense paper liner substrates from emulsion or dilute solution in aromatic and aliphatic solvent. Market demand for reduction in solvent led to heat-cured 100% silicone solids release coatings[2]. UV- and EB- curable solvent-free silicone release agents were subsequently introduced for use on thermally sensitive film liner substrates and in other niche markets. High speed coating technology has kept pace with silicone chemistry so that less than1 micron thick defect-free silicone coatings are routinely applied and cured on papers and films at line speeds exceeding 1000 meter/minute (this corresponds to production of about 300 miles of release liner in an 8 hour shift).

Background: How are Release Liners Tested?

Given the complexity of coating processes and curing chemistry for high speed application and subsequent conversion of liquid silicone formulas to solid abhesive coatings, there are numerous test protocols in use to determine the quality and performance characteristics of silicone release agents. The *coating quality and consistency* is assessed by measuring the coatweight (silicone deposition) at several different spots on the liner exiting the cure station. Silicone deposition is most often determined by X-ray fluorescence techniques and is recorded as a function of position across the web width. *Quality of Cure* includes adhesion of the silicone coating to substrate, presence of uncured ('loose') silicone polymer in the cured coating and the degree of crosslinking. Simple finger smear across the silicone is a good qualitative test for substrate anchorage and presence of uncured silicone. When pressed into the silicone coating surface, aggressive pressure sensitive tapes will no longer stick to themselves if unreacted loose silicone is transferred from the coating. Extraction of a known area of liner with solvents such as MIBK or heptane dissolves silicone that is not crosslinked into the coating; gravimetric, atomic absorption, and XRF techniques are then used to quantify the percentage of 'loose siloxane' in the coating. Finally, the *Quality of Performance* is defined by release testing.

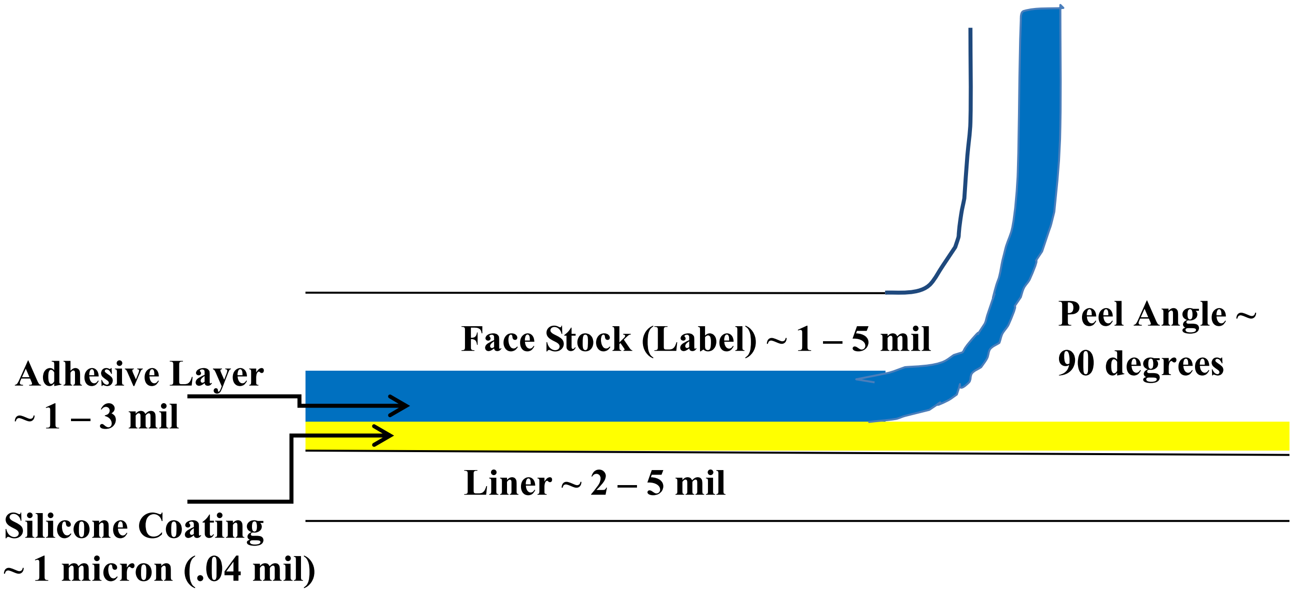


Figure 3: Illustration of Peeling an Adhesive Label from Release Liner

Release is defined as the work or force required to peel the facestock/adhesive lamina away from the liner or peel the liner from the facestock at a specified speed and angle. Force (in grams) per unit of width (cm or inch) is normally used to define release performance. For example, 5g/in is considered 'easy', or low release; 200 g/in is considered tight or high release. Instruments are used to precisely measure release of pressure sensitive laminate constructions that are slit into tapes of fixed widths.

Cationic Photocurable Silicone Release Compounds

Given that silicone release coatings are very thin, transparent fluids applied to flat web substrates, they are excellent candidates for UV or EB cure. Radiation curable silicones include reactive functionality that replaces some of the methyl groups attached to silicon along the -O-Si-O-Si- backbone of linear PDMS. Thus, polysiloxane analogs of organic radiation curable coatings were developed that combined the unique properties of silicone with the near instantaneous crosslinking of radiation curable coatings. In particular, *acrylate* functional silicones were developed as free-radical UV and EB curable release coatings[3-5] while *cyclohexyl epoxide* functional silicones were found to be radiation curable in the presence of certain cationic 'onium type catalysts[6]. The structure of a typical cyclohexyl epoxy silicone (generally referred to as an 'epoxysilicone') derived from reaction of 4-vinylcyclohexeneoxide with preformed SiH functional silicone[7] is shown in Figure 4:

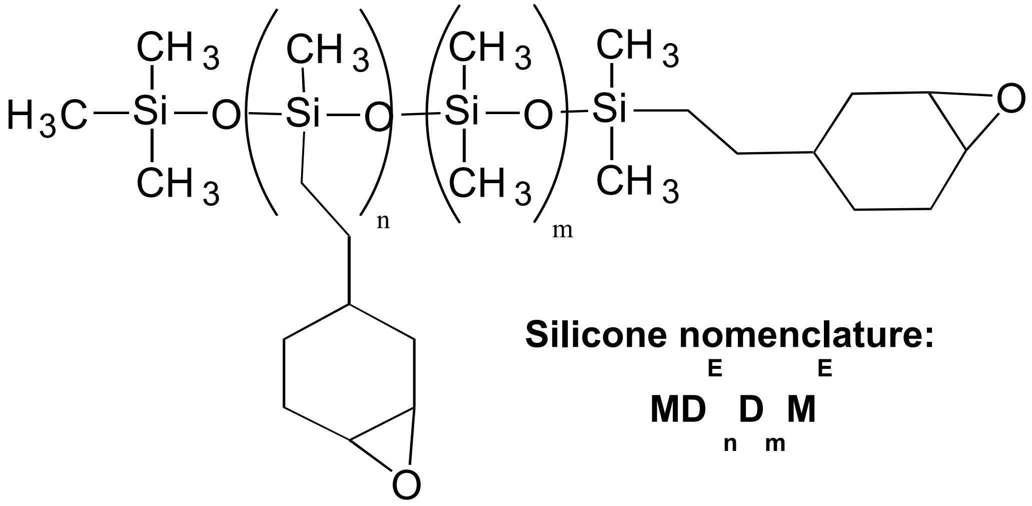


Figure 4: Epoxysilicone Polymer, n=2-10, m=50-150

Strong acids resulting from photodecomposition of sulfonium and iodonium compounds catalyze very rapid ring opening polymerization of strained ring oxiranes such as the cycloaliphatic epoxy groups pendant on epoxysilicone polymers. This process 'cures' the liquid silicone coating into a solid *abhesive* release coating, the structure of which is depicted in Figure 5 below. The crosslinked structure is a short chain poly(cyclohexylether) to which polydimethylsiloxane segments are attached. Since PDMS has very low surface energy, the coating is oriented such that the silicone component is at its surface, allowing the cured coating to release pressure sensitive adhesives in contact with it.

Design of the epoxysilicone determines how well the coating releases tacky organic PSA's, glues, mastics, asphalts, etc. If too much organofunctional epoxy is present the crosslinked coating is a high modulus clearcoat that *adheres* to an adhesive rather than releases it. If too little reactive epoxy character is extant the coating will not cure quickly or well. The level of epoxy content is also critical to miscibility with polar 'onium salt photocatalysts.

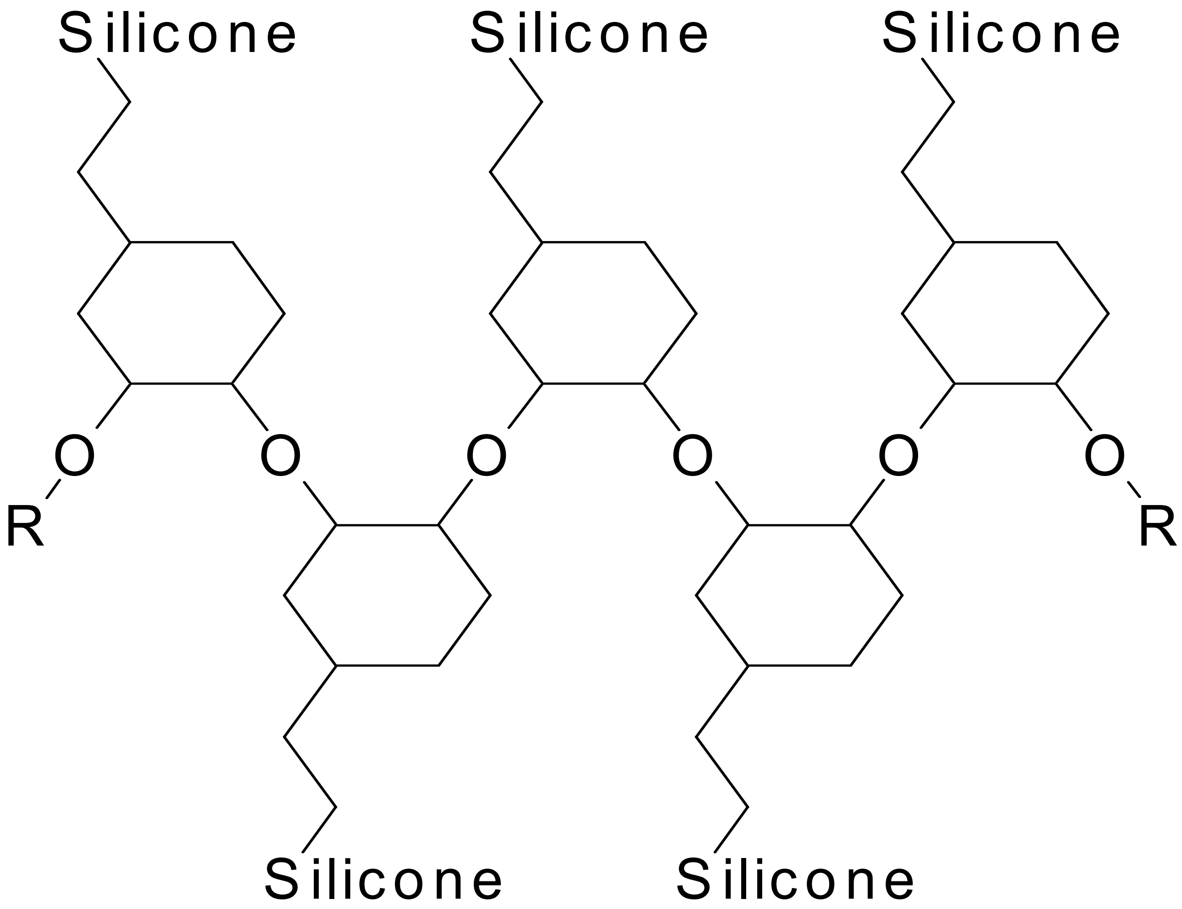


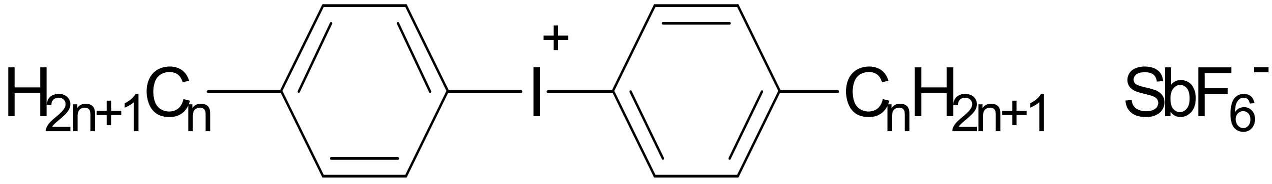
Figure 5: Depiction of Structure of Cured Epoxysilicone Release Coating

‘Onium Salt Photocatalysts for Cationic UV Curable Silicones

The photodecomposition of various poly(phenyl) sulfonium $[Ph_xS_y]^+$ and di(phenyl) iodonium $[Ph_2I]^+$ salts was described in literature articles dating back to the late 1950’s. If the salt’s associated anion is strongly electron withdrawing such as $[PF_6]^-$ or $[SbF6]^-$ then irradiation leads to generation of ‘superacid’ species that initiate rapid polymerization of vinyl ethers, oxiranes, oxetanes, furans, and other reactive compounds. Research carried out independently at 3M and General Electric demonstrated the feasibility of photocurable compositions consisting of dispersions of these ‘onium salts in acid-sensitive reactive organic monomers and oligomers[7-9]; it was also confirmed that photocure with sulfonium and iodonium catalysts is not inhibited by oxygen, a very useful property. However, when chemists tested polar sulfonium and iodonium salts as photocatalysts for crosslinking epoxysilicone polymers, very poor results were observed due to the poor miscibility of unsubstituted phenyl sulfonium and iodonium compounds in reactive silicone media; this was *particularly* true of sulfonium salts.

So, successful design of commercial cationic type radiation curable silicone coatings required modifications of 'onium salts to make them dispersable in epoxysilicone polymers. Given the greater polarity of sulfonium salts vs. iodonium analogs, these efforts focused on iodonium compounds.

Symmetrical diphenyl iodonium salts $[(C_6H_5)_2\,I]^+\,X^-$ ($X = PF_6$, AsF_6, SbF_6) are crystalline solids with sharp melting points above 120 °C; these catalysts are immiscible in PDMS fluids as well as all epoxysilicones tested. Replacing the phenyl group attached to iodine with a 4-alkyl phenyl reduces the crystallinity of symmetrical iodonium PF_6 and SbF_6 compounds and increases their lipophilicity. When the 4-alkyl group was derived from a *mix* of different long chain hydrocarbons referred to as 'linear alkylate' dodecylbenzene (Figure 6) the resulting product is a blend of about 108 discrete compounds[10] without a fixed melting point:



'C_nH_{2n+1}' is mixed alkyls, $n \sim 10 - 14$

Figure 6: Symmetrical iodonium photocatalyst structure

The iodonium compound displayed in Figure 6 is sufficiently compatible with epoxysilicone polymers to promote rapid photocure[6], though complete solubility is only possible beyond a certain threshold of epoxy content in the silicone. Asymmetrical iodonium salts with alkoxy groups tied to one of the benzene rings were developed that are generally non-toxic and quite soluble in non-silicone cationic curable media[11], but these compounds do not dissolve in epoxysilicone polymers without high levels of reactive diluent present in the coating formulation, which is not practical for premium release liners.

A different strategy proved to be more successful: rather than trying to make the iodonium radical lipophilic, researchers looked at the *anion* to increase charge separation, reduce salt polarity, and thereby improve catalyst compatibility with nonpolar cationic cure media.

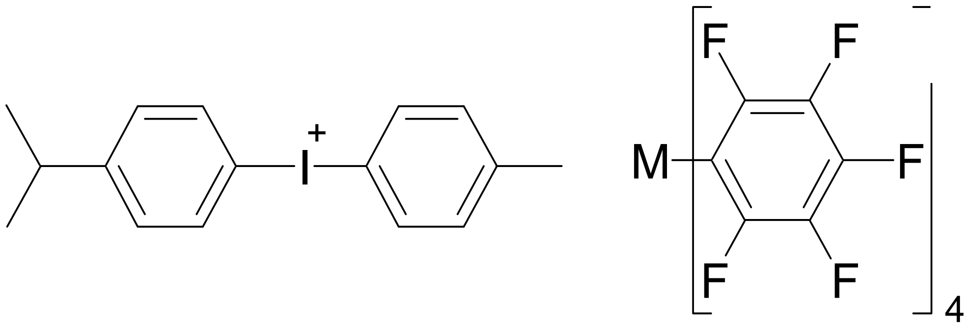
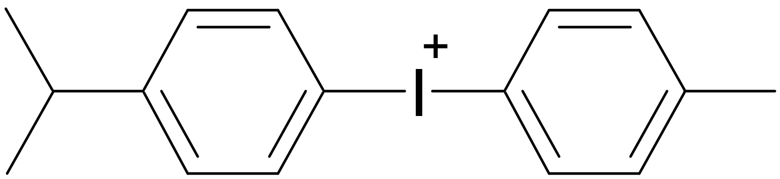


Figure 7: Iodonium Photocatalyst with Anion Containing Pentafluorophenyl Groups; M = B, Ga

Attaching strongly electron withdrawing $[(C_6F_5)]$ groups to borate[12] or gallate[13] anions dramatically alters the polarity and solubility characteristics of iodonium salts. Figure 7 depicts the structure of these catalysts where M = B or Ga. A different variation on this theme is to attach multiple $[B(C_6F_5)_3]$ groups to an imidazolate anion[14] giving rise to a high MW catalyst with widely dispersed charge. These iodonium imidazolate salts are very soluble in a wide range of epoxysilicone polymers and promote excellent cure and release performance. Such highly fluorinated iodonium catalysts overcome the inherent incompatibility of polar salts with PDMS polymers and are excellent catalysts for radiation cure of epoxysilicones, but their cost and the complexity of syntheses of $[M(C_6F_5)_x]_y$ containing compounds plus their high molecular weight (> 1000 Daltons MW means that *mole%* of these catalysts is quite low at normal wt% load in coating baths) have limited their use to specialty markets.

Novel Iodonium Catalysts for Silicone Coatings



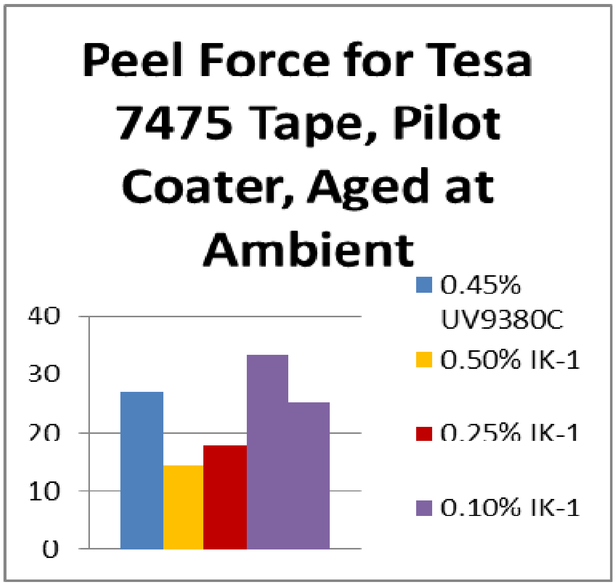
$[P(C_nF_{2n})_xF_{6-x}]^-$

Figure 8: Iodonium Photocatalyst Containing Fluoro and Fluoroalkyl Groups

Research into ionic liquids based on ‘onium salts of fluorinated anions has been widely published, including an article describing the syntheses of (perfluoroalkyl) fluorophosphate salts of various cations[15]. A photocatalyst bearing such an anion has been developed[16] as shown in Figure 8.

Structural advantages of such a catalyst include high fluoro content (where n=2 and x=3, F ~ 40% of the formula), stability as a neat crystalline solid, and relatively low molecular weight, making the catalyst typically more efficient as a function of weight. We have confirmed the efficacy of this type of iodonium catalyst for cationic UV cure of silicone coatings. When tested, these new compounds proved compatible with epoxysilicone polymers, and, combined with certain sensitizers they provide for very efficient cationic photocure of commercial epoxysilicone release agents when applied to film and film laminate liners as described below.

Comparative cure studies of a commercially available sensitized iodonium catalyst, UV9380C[17], versus an iodonium perfluoroalkyl fluorophosphate catalyst (called IK-1, provided by San Apro, Ltd) were carried out. The commercial catalyst was used as furnished and the neat solid IK-1 was dissolved in IPA before each photocatalyst was dispersed into an epoxysilicone release agent, UV9400[17]. The catalyzed coating baths were applied to a New Page clay coated paper substrate on a pilot coating line equipped with a three roll offset gravure coating head and one bank of focused microwave fired 300 Watt/in medium pressure mercury vapor H lamps. Coater liner speed was held at 300 feet/minute; coat weight of ~ 1.4 g/m^3 was targeted. tesa™ 7475 acrylic PSA test tapes (tesa is a trademark of tesa SE) were pressed into the cured silicone coating immediately off line. Liner samples with tapes attached were aged for 20 hours at room temperature and at 70 °C before the force required to peel the liner from the tape at 300 in/minute peel speed was recorded. Release results are graphically displayed in Figure 9.



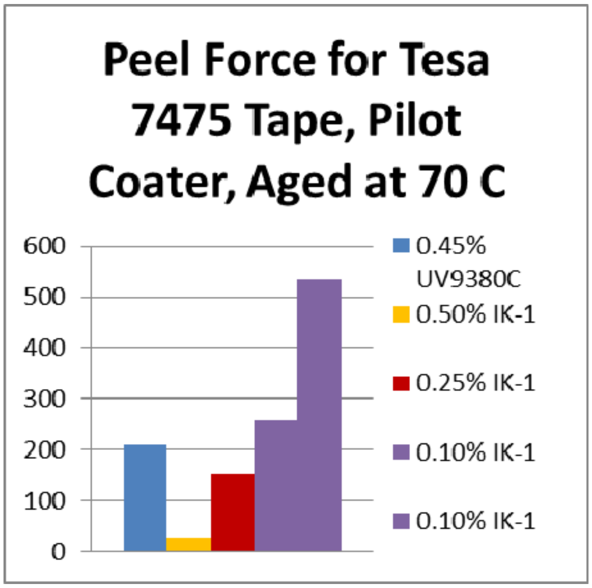


Figure 9: Peel Force of Tapes from Epoxysilicone Liner Catalyzed with IK-1

The y axis of each graph is release measured as gram/inch; note how much the release rose when the tape/liner construction was oven-aged. This experiment is a harsh test of cationic photocatalyst efficacy because photocure of epoxysilicone coatings is difficult on basic substrates, including most papers and particularly clay coated kraft sheets. What we observed was that an IK-1 concentration slightly more than *half* that of the iodonium content of UV9380C catalyst provided lower and more stable release, and that a solids basis of 0.5% IK-1 overcame the basicity of the clay-coat liner. A secondary observation is that UV9380C made a very hazy mix in UV9400 polymer, while comparable concentration of IK-1 dissolved to a clear solution.

Similar coating baths were then applied to the same substrate on a different coater equipped with two banks of Fusion H lamps and capable of much faster line speed. Tesa7475 test tape was applied to the cured silicone coating on clay-coat sheet a day after photo-exposure; the applied tapes were then aged at ambient conditions and at 70 °C before release of liner from test tape was determined. Results are depicted in Figure 10.

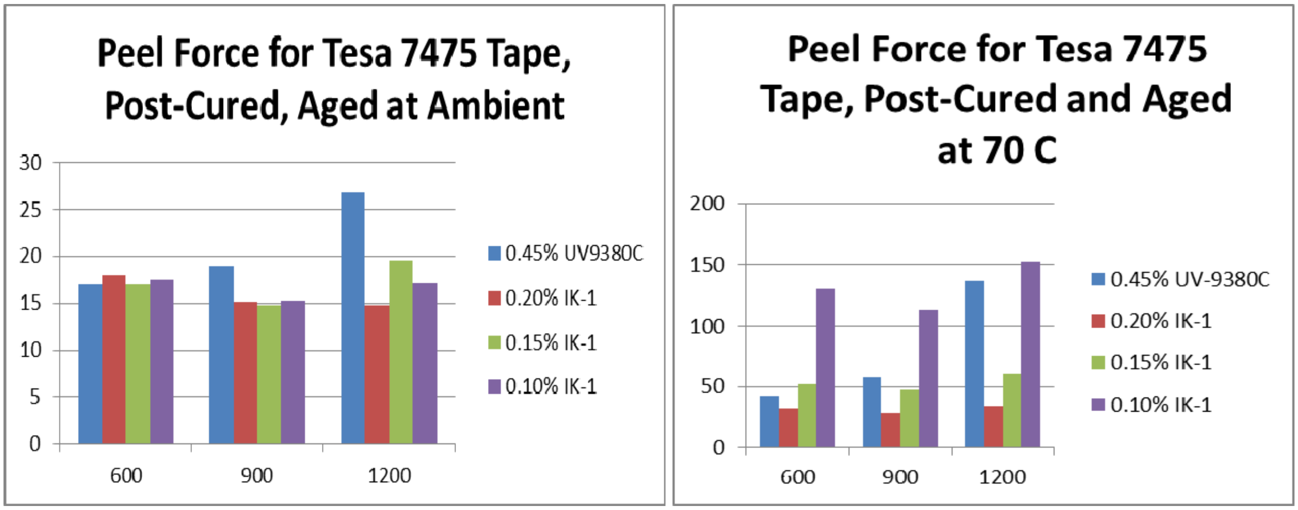


Figure 10: Peel Force of Tapes Peeled From Epoxysilicone Release Liners Catalyzed with IK-1 as a Function of Coater Line Speed

As in Figure 9, the y axis is release force required to peel liner from the test tape, measured in g/in. The x axis refers to line speed in ft/minute; the coating line was run at 600, 900, and 1200 ft/minute; exposure time and incident UV flux at 1200 fpm was about half of the previous experiment run at 300 fpm with one bank of H lamps. Oven-aging of the taped liner led to significant build in release, but the perfluoroalkyl fluorophosphate salt at 2000ppm concentration performed as well or better than the commercial catalyst at all line speeds tested; stability was lost at 1000ppm of the IK-1 catalyst.

Anthracene sensitizers for Cationic UV Cure Silicone Coatings

Iodonium salts are strong UV absorbers in the ‘C’ (short wavelength UV) section of the UV spetrum, with little photoresponse to lamp emission >300 nm; the large 313nm and 365nm peaks of the medium pressure Hg lamp spectrum are not absorbed. Hence, sensitizers are used to improve system efficiency and permit use of longer wavelength ‘D’ or High pressure mercury vapor lamp sources. Thioxanthones including isopropylthioxanthone (ITX) are well known sensitizers for iodonium-catalyzed UV cure of epoxysilicones. Prior work had demonstrated that anthracene moieties could be reacted into epoxysilicone polymers, thus creating fluorescent coatings that were self-sensitized[18]. As part of our photocatalyst studies we included comparitive cure experiments to determine if 9,10-dialkoxyanthracene compounds were as effective sensitizers as ITX for cationic UV cure of epoxysilicone release coatings. The following catalyst dispersions were made up in IPA and are displayed in Table 1.

Table 1: Catalyst blends Used for Cure Study

Catalyst blend	**Catalyst, %**	**Sensitizer, %**
A	**Iodonium borate, 27.7%**	**DEA, 2.8%**
B	**Iodonium borate, 28.5%**	**none**
C	**IK-1, 27.7%**	**DEA, 2.8%**

In Table 1, ‘Iodonium borate’ is tolyl-cumyl iodonium tetrakis(perfluorophenyl) borate (Figure 7) and DEA is 9,10-diethoxy anthracene. 1 or 2 parts of catalyst solutions A, B, and C were mixed with 100 parts of UV9400 epoxysilicone polymer; a blend of 2 parts UV9380C catalyst with 100 parts UV9400 was also prepared as a control. All catalyzed coatings were applied to a 2 mil PET film substrate, cured and release tested with tesa^{TM} 7475 test tape as described above. Release performance was assessed as a function of coater line speed, with results displayed in Figure 11.

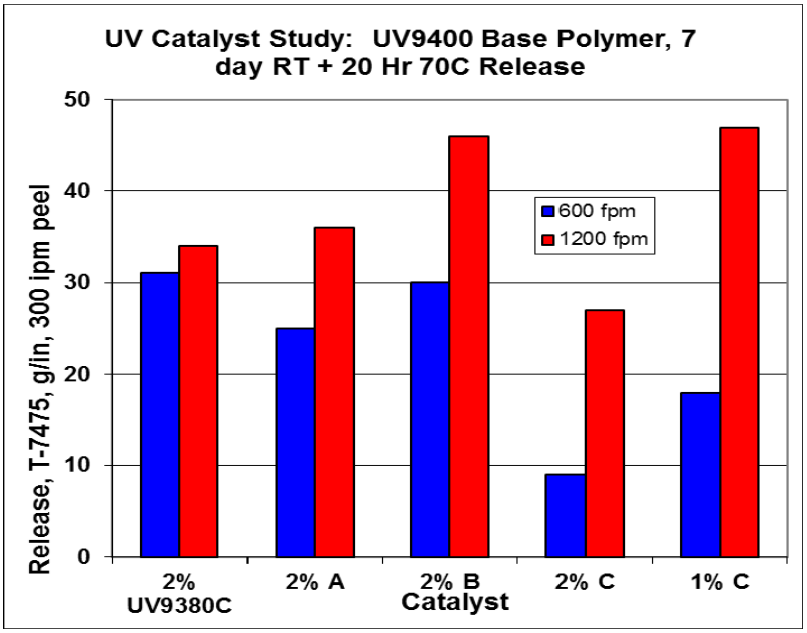


Figure 11: Effect of Photocatalyst and Photosensitizer on Release Force

These results indicate that DEA sensitizer improved photoresponse of the iodonium borate catalyst in an epoxysilicone medium and can be a good additive for use with the IK-1 catalyst, too. It should be noted that the commercial UV9380C iodonium catalyst solution included ITX. IK-1 proved to be superior to the iodonium borate catalyst as well as UV9380C catalyst in this particular experiment.

Concluding Remarks

The goal of this presentation is to introduce the basics of silicone release coatings and of radiation curable silicone coatings to the general RadCure audience. Cationic UV curable silicone release coatings require silicone compatible 'onium salt catalysts capable of promoting rapid on-line cure of liquid silicone to highly crosslinked abhesive coatings useful for release of pressure sensitive adhesives found in label construction. New iodonium perfluoroalkyl fluorophosphate catalysts in combination with dialkoxy anthracene sensitizers have been found to be very effective for efficient photocure of epoxy-functional silicones. It is expected that continuing development of 'onium salt catalyst technology will further improve radiation curable silicone release coating systems.

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