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► **To cite this version:**

Alexei V Radchenko, Francois Ganachaud. Photocatalyzed Hydrosilylation in Silicone Chemistry. Industrial and engineering chemistry research, 2022, 61 (23), pp.7679-7698. 10.1021/acs.iecr.2c01015 . hal-03762360

HAL Id: hal-03762360

<https://hal.science/hal-03762360>

Submitted on 27 Aug 2022

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Photocatalyzed hydrosilylation in silicone chemistry

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KEYWORDS: Hydrosilylation, Photoactivation, Photocatalyst, Silicones, 3D printing

ABSTRACT. Hydrosilylation is widely used in silicone chemistry to crosslink formulations so as to generate elastomer materials. Most often, heat is the easiest way to activate a platinum catalyst that proceeds to reaction, but photoirradiation is an alternative way to promote hydrosilylation in a fast and mild way. The open and patent literatures dealing with light-induced hydrosilylation are exhaustively reviewed here. First, various promoters, including metal (photo)catalyst, co-catalysts and inhibitors, are systematically described. Some kinetics provided by the very few available academic papers are disclosed as well. Throughout the review, proposed applications, mainly in coatings, are reported, whereas potential applications in 3D printing are specifically disclosed as a separate final chapter. Prospects about the pros

and cons of the photohydrosilylation technique compared to other irradiation-promoted catalytic systems used in silicones, close the article.

1. Introduction

Hydrosilylation is a well-studied reaction occurring between hydrogen-silicon bond and a multiple bond¹; a general scheme of hydrosilylation using an example of alkene and silane is presented in Figure 1a. Since the second half of the 20th century, hydrosilylation has found many applications in organic² and in polymer chemistries³. The complexes of such transition metals as platinum², rhodium^{4,5}, ruthenium⁶⁻⁸, palladium^{9,10}, nickel¹¹, iron¹² and iridium^{13,14} were described as catalysts for this reaction; most commercially used are the complexes of platinum, typically Karstedt's and Speier's catalysts (see structures in Figure 1b)³.

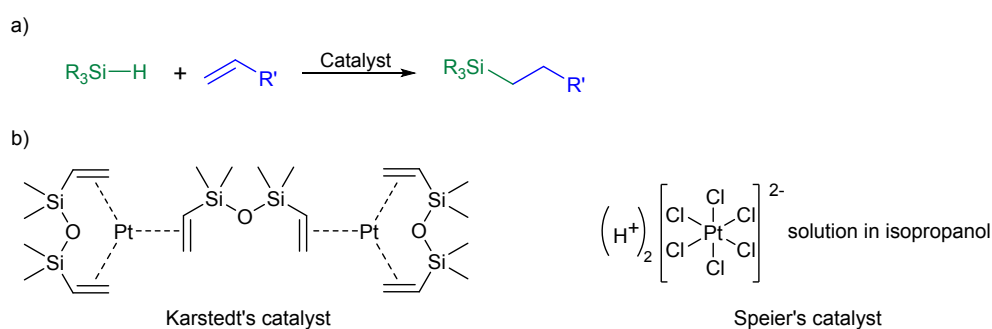
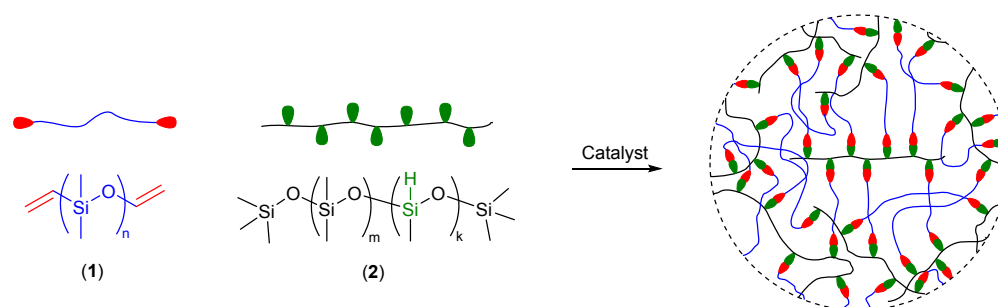


Figure 1. General scheme of alkene hydrosilylation (a) and most often used catalysts (b).

In polymer chemistry, hydrosilylation is widely applied to the production of crosslinked silicone elastomers (Figure 2). Usually long divinyl-terminated poly(dimethylsiloxane) chains (**1**) (divinyl-PDMS) are crosslinked by adding oligomeric crosslinking chains such as poly(dimethylsiloxane-co-

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2 methyl-hydrogenosiloxane) (2)¹⁵ and very small quantities (5–10 ppm) of Pt-catalyst³. Final materials
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5 are generally characterized by improved chemical and temperature resistances, and better mechanical
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8 properties (tensile strength, tear strength, gas permeability) than silicones obtained by other
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11 crosslinking methods³. Moreover, the low toxicity of employed catalysts allows using these materials
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15 in biomedical and healthcare applications¹⁶.



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30 **Figure 2.** Typical example of hydrosilylation-based crosslinking of silicones.

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35 One particularly interesting method of polymer crosslinking is radiation curing (for recent reviews
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37 on polysiloxane radiation curing, see^{17,18}). Usually, crosslinking through light, electron beam or
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39 gamma irradiation leads to shorter curing time, less heat generation and, in case of the latter two,
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42 without requiring the use of metal catalyst,¹⁷ making the process particularly economical in e.g. fast-
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45 curing of films. For photoinitiated curing, silicone oils are functionalized by various groups, e.g.
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48 acrylate, thiol, epoxide, or vinyl^{15,18} and crosslinked by radical or cationic means. One main
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Thiol-ene curing can partly overcome these limitations¹⁹, but a major disadvantage of mercaptans is

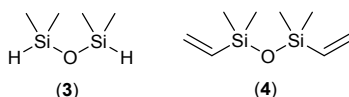
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2 their strong unpleasant odor¹⁵. Cationic crosslinking is fast²⁰ but highly sensitive to moisture and still
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5 proceeds after the light is off (which may be good or not, depending on the technology developed).
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8
9 In all these processes, the presence of organic (non-silicone) crosslinks may limit the thermal stability
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12 of obtained materials.
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16 Hydrosilylation-cured silicone elastomers usually do not show these disadvantages (short ethylene
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18 bridges formed by hydrosilylation do not have limitations of other organic crosslinks) and there are
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20 photoactive catalysts that are available for photocuring of silicone oils. Surprisingly, up to now, there
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22 has been no review on photohydrosilylation in polymer chemistry, despite a significant number of
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27 patents and scientific article published in the past 50 years. In contrast to photoinduced
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33 hydrosilylation in organic synthesis that has been reviewed²¹, photohydrosilylation in polymer
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38 chemistry was usually cited only as a small part in larger reviews of hydrosilylation^{3,22} and did not
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42 cover exhaustively published materials. Here, we review the topic of light-induced hydrosilylation
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2. Preliminary works on silicone photohydrosilylation.

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2 The present section describes early basic studies where non-photoactive catalysts or simple radical
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6 initiators were used together with powerful lamps. To our knowledge, the first example of
7
8
9 photocatalyzed hydrosilylation involving siloxanes was reported by Faltynek in 1981²³ who used
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11
12 1,1,3,3-tetramethyldi-siloxane (3) and 1,3-divinyltetramethyl-siloxane (4) (Figure 3) as model
13
14
15 compounds to study the photocatalytic activity of rhodium (I) complexes with phosphine and
16
17
18 phosphite ligands. It was shown that in the presence of $\text{ClRh}(\text{O}_2)(\text{PPh}_3)$ in benzene or cumene,
19
20
21 hydrosilylation occurred faster under irradiation at 366 nm than in the dark, even if the reaction
22
23
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25
26 required several hours.



34 **Figure 3.** Model siloxanes for photohydrosilylation described in²³.

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36
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38 Many examples of early crosslinked polysiloxane synthesis by photohydrosilylation can be found
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40
41 in the patent literature. General Electric (GE) Company developed coatings based on polysiloxane
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43
44 containing different amounts of methylvinylsiloxo, methylhydrogenosiloxo and dimethylsiloxo
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47 units²⁴. They used tert-butyl peroxybenzoate (5, Figure 4) as a radical initiator for curing under 160
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60 w/cm high pressure mercury lamp (UV-7000 from Ushio Electric Co., Ltd.). The adhesion of obtained
coatings to different substrates was excellent, contrary to comparative examples where

methylvinylsiloxy or methylhydrogensiloxy units were omitted. This result may indicate that crosslinking happened by hydrosilylation reaction as Si-H and vinyl groups are necessary here.

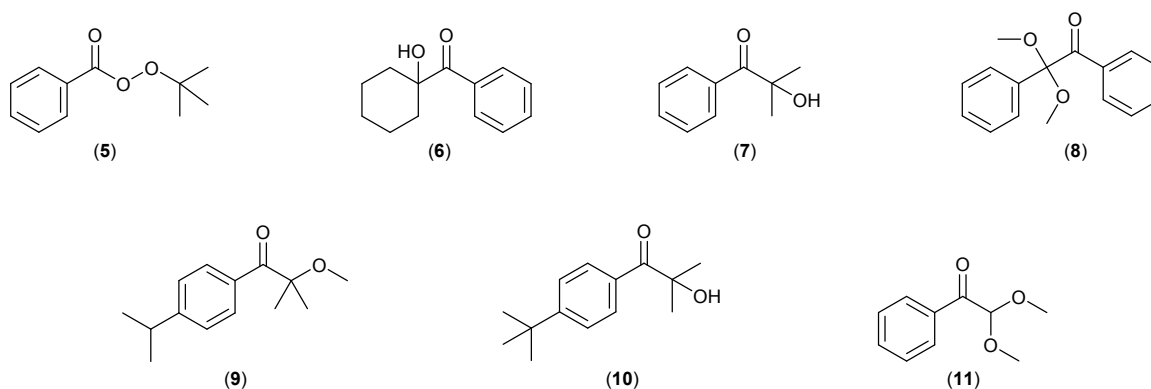


Figure 4. Radical (photo)initiators employed to promote hydrosilylation in reviewed publications.

Shin-Etsu Chemical Co., Ltd. reported photohydrosilylation of several vinyl-containing silicone oils (1, 12 – 14) with poly(methylhydrogensiloxane) (15) (Figures 2 and 5)²⁵. The inventors refer to the employed catalyst as “platinum-vinylsiloxane complex” without any information about its structure or composition. It may correspond to the well-known Karstedt’s catalyst²⁶ that is not usually considered as a photoactive one.

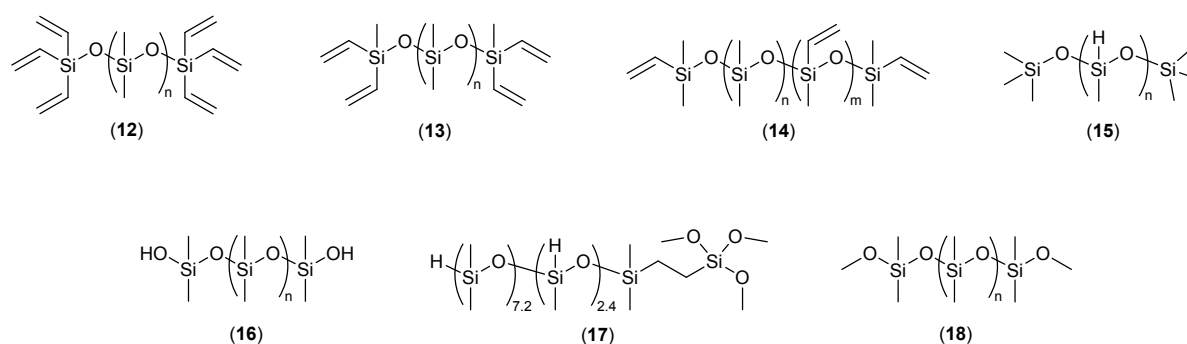


Figure 5. Silicone oils described in this review as components of photohydrosilylation formulations.

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2 Nevertheless, the formulations containing above-mentioned silicone oils and catalyst (150 ppm of
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5 Pt) were used to prepare coatings by photocuring the samples at a distance of 8 cm under two high
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9 pressure mercury lamps each having an output of 2 kW and a linear output density of 80 W/cm. It
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12 was clearly shown that the various vinyl-containing silicones present different activity in the
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15 described conditions. The least active divinyl-PDMS (1) based coating required 10 sec of exposure
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18 to obtain a tack-free surface, while for the most active one, bis(trivinylsilyl)-polydimethylsiloxane
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21 (12), only 0.6 sec of exposure was sufficient to remove the tackiness. In the same patent²⁵, it was
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24 shown that adding ceric oxide (CeO₂) could accelerate hydrosilylation reaction under UV-light: a
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27 formulation containing 2.8 wt.% of this compound was cured in an impressive 0.4 sec. Also, this
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30 company presented a similar study using Speier's catalyst (H₂PtCl₆) in the presence of
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33 photosensitizers 19 and 7 (Figures 4 and 6)²⁷. Using the same UV lamp and the silicone oils described
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36 in the previous patent, they obtained extremely quick curing times (between 0.1 and 2 sec).
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39 Unfortunately, for both catalysts, there is no information about dark curing, shelf life or possible
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42 heating of the formulations below the powerful UV lamp. For H₂PtCl₆-based system, a blank
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45 experiment without sensitizers was also missing. Such data would be interesting to clarify whether
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48 these catalysts have photoactivity or if they have been activated by the heat of the UV lamp.
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3. Photohydrosilylation with diene-Pt complexes.

3.1. Patent literature.

Minnesota Mining and Manufacturing (3M) Company patented UV-activated hydrosilylation between divinyl-PDMS (**1**) and poly(methylhydrogenosiloxane) (**15**) using Pt complexes bearing 1,5-cyclooctadiene (COD) and aromatic ligands (**41** – **60**, Figure 7)²⁸. They prepared formulations containing 180 ppm of platinum to hand coat them on polyester film and study photohydrosilylation. They used 20 watt “black” light lamp at a distance of 2.5 cm and measured the time required to convert the coating to a non-smearing surface. For almost all formulations, from 2.5 to 4.5 min were required. The only two exceptions were i) the complex bearing perfluorophenyl ligand (**49**) that required 15 min to cure under irradiation and ii) the one bearing 4-dimethylaminophenyl (**55**) that cured the resin in the dark in 4 minutes (and was thus not tested under UV-light).

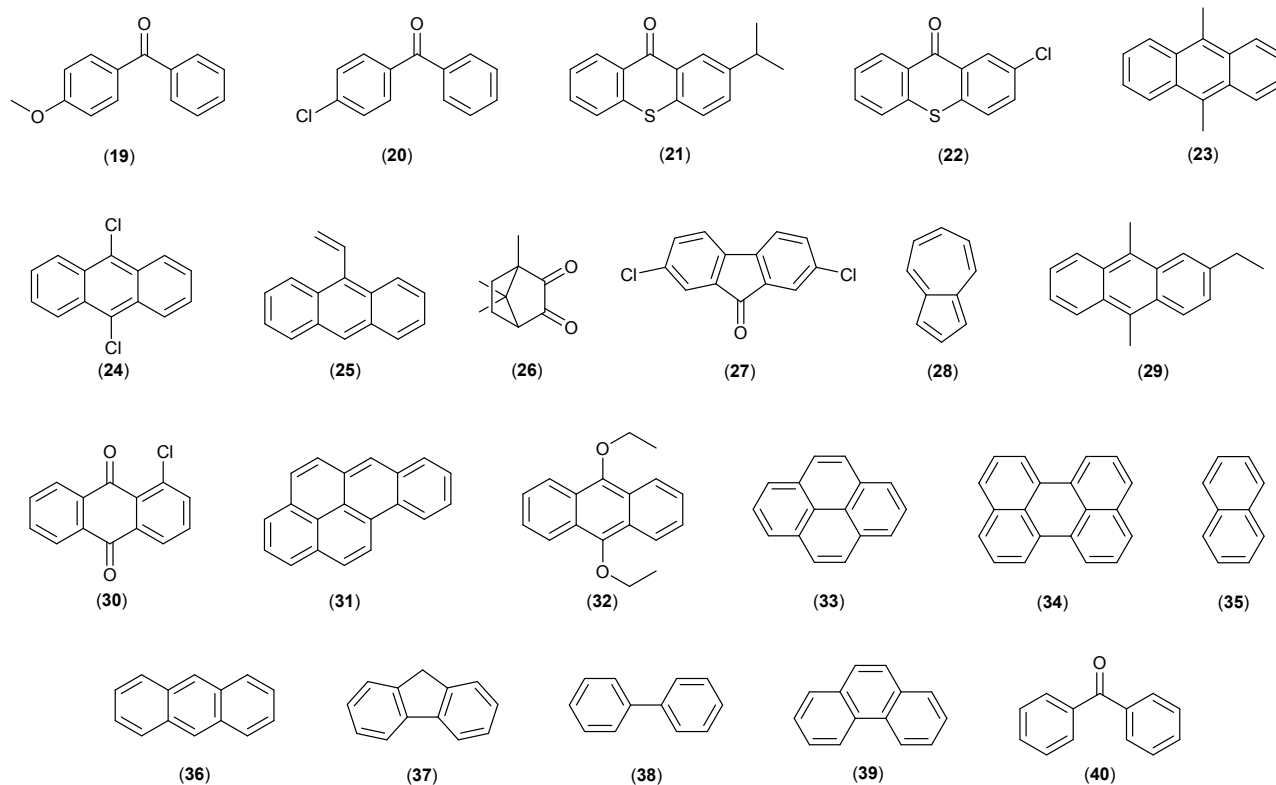


Figure 6. Structures of the compounds tested as photosensitizers in photohydrosilylation systems mentioned in this review.

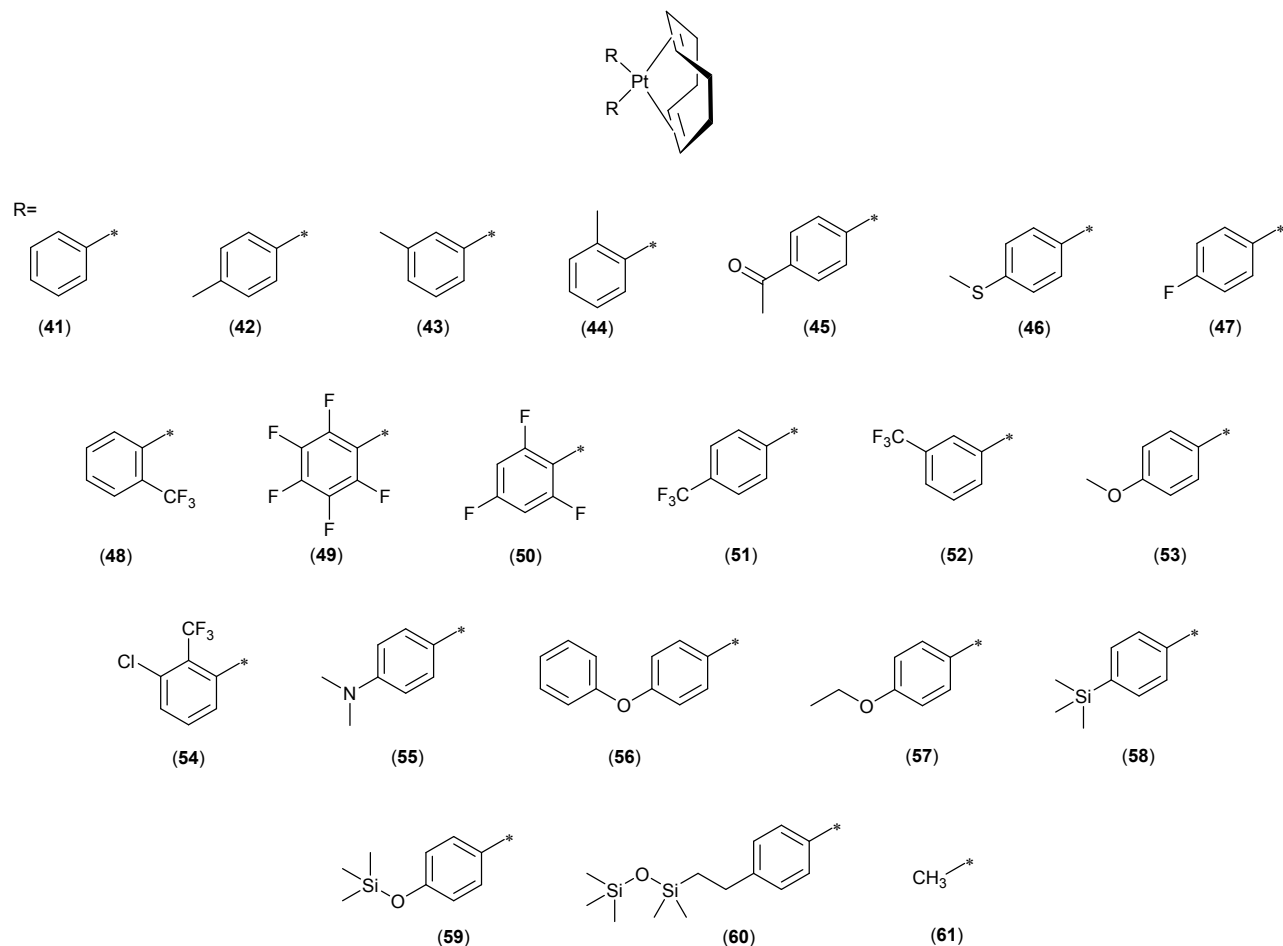
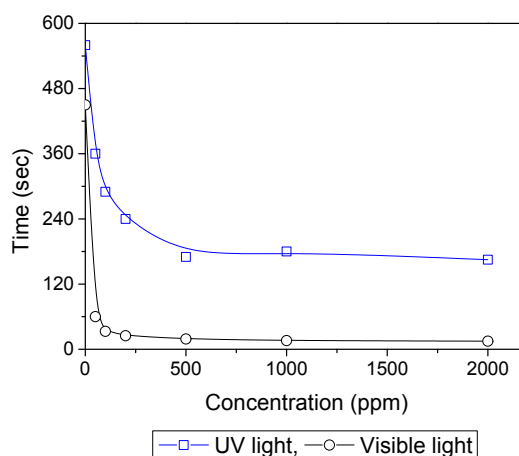


Figure 7. COD-Pt complexes used as photohydrosilylation catalysts in²⁸⁻³².

The catalytic activity of four of these Pt-complexes (di(4-methylphenyl)-Pt(COD) (42), di(4-trifluoromethylphenyl)-Pt(COD) (51), di(4-methoxyphenyl)-Pt(COD) (53) and di(4-trimethylsilylphenyl)-Pt(COD) (58), 200 ppm Pt content) was studied in the presence of a number of photosensitizers (20 – 28, Figure 6, 500 ppm)²⁹. The curing was performed under UV-light (six 15 watt “black” light lamps, maximum output at 365 nm) as well as under visible light (“Visilux” 2

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2 dental curing light, wavelength 400 – 500 nm). The power of visible light source is not mentioned in
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6 the patent, which does not allow to compare the efficiency of these two types of irradiation. For
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9 fluorine- and silicon-containing catalysts (51, 58), the tested additives (22, 23) only slowed down the
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12 reaction under both sources of light, while for other Pt-complexes, certain sensitizers provoked an
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15 accelerating effect. The most pronounced sensitizing effect was achieved for the couple di(4-
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17 methoxyphenyl)-Pt(COD) (53)/2-chlorothioxanthone (22), the time required to obtain tack-free
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19 polymer was reduced from 530 to 172 sec under UV-light and from 480 to 25 sec under visible light.
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26 The influence of sensitizer concentration was studied for this system ((53)/(22), see Figure 8). It can
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29 be seen that cure time decreased with an increase of sensitizer content up to 500 ppm, while further
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32 increasing this concentration did not noticeably accelerate the reaction.
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1
2 **Figure 8.** Influence of 2-chlorothioxanthone (**23**) concentration on the required time to cure silicone
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6 formulation in the presence of 200 ppm of di(4-methoxyphenyl)-Pt(COD) (**53**) under UV (365 nm)
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9 and visible (400 – 500 nm) light²⁹.

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13 Later, a similar but simpler catalyst ((COD)PtMe₂) (**61**, Figure 7) was employed by inventors from
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16 Shin-Etsu Chemical Co., Ltd. to produce silicone templating mother molds³⁰ (the term “mother mold”
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19 is used in the patent to refer to the mold obtained by casting around a master model). The formulation
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22 contained 30 ppm of Pt and no additional components apart from vinyl and Si-H containing MQ-
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25 resins (highly branched silicone resin³³) and divinyl-PDMS (**1**). The composition was cured for
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30 10 min (2.0 J/cm²) in a rectangular exposure chamber where 40-W fluorescent lamps emitting UV
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33 light at a center wavelength of 370 nm were disposed at each wall (six lamps overall). The obtained
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36 sample were characterized by hardness of 34 Shore A, elongation of 400 %, tensile strength of
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39 3.4 MPa, tear strength of 7.4 N/mm and light transmittance at 370 nm of 36 %. The formulation was
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43 utilized to obtain molds that were successfully used to replicate a model.

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46 The 3M Company proposed another method of UV-activated silicone hydrosilylation by using a
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49 new type of platinum catalyst containing cyclopentadienyl (Cp) or its derivatives as a ligand (**62** –
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52 **70**, Figure 9)^{34,35}. Cyclopentadienyl-platinum complexes are known to well absorb UV light³⁶. The
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55 gel-time (time required to achieve a state in which the resin no longer flows) under “black” light (20
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58 watt) was measured between 16 and 40 sec for these catalysts (Pt concentration 200 ppm), while
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2 without irradiation at room temperature, the gel time was 30 h for (methoxycarbonyl-Cp)-
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5 trimethylplatinum (**68**) (most active) and more than 1550 h for (Cp)trimethylplatinum (**62**).
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9 Interestingly, it was also shown that the crosslinking of these formulations can occur in the dark after
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11 exposure to “black” light: after 10 sec of exposure, it took from 16 to 160 sec to reach the gel point,
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15 depending on the catalyst.
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19 In a following study, the same company modified the system based on (Cp)trimethylplatinum (**62**)
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21 to use it for visible light curing (“Visilux” 2 dental curing light, wavelength 400 – 500 nm)³⁷. Several
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23 photosensitizers were tested to accelerate curing, the most effective ones being 2-chlorothioxanthone
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26 (**22**), 9,10-dimethylantracene (**23**), 9,10-dichloroanthracene (**24**), 2-ethyl-9,10-dimethylantracene
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29 (**29**), 1-chloro-anthraquinone (**30**), benzo[a]pyrene (**31**) and 9,10-diethoxyanthracene (**32**) (see Figure
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6). The inventors measured the time of exposure required to get tack-free polymers in the presence
of 960 ppm of Pt, which is quite concentrated. They found that 2-chlorothioxanthone (**22**) was again
the most active photosensitizer in these conditions, for which only 33 sec of exposure were required
(compared to 117 sec for the formulation without photosensitizer). Also, it was shown that in the
presence of 9,10-dimethylantracene(**23**), the cure speed could be enhanced by increasing the
platinum content up to 2000 ppm; further addition of the catalyst almost did not accelerate the
reaction. Moreover, the influence of sensitizer concentration was studied with 2-ethyl-9,10-
dimethylantracene (**29**). It was found that an increase of concentration from 200 to 1500 ppm led to

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2 a decrease in required cure time from 77 to 37 seconds; higher concentrations of sensitizer were not
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6 tested. The use of such photocurable resin for preparation of dental impressions was described in this
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9 patent. For this purpose, the formulation of silicone oils (divinyl-PDMS (1) and
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12 poly(dimethylsiloxane-co-methylhydrogenosiloxane) (2)) with 900 ppm of platinum, 1000 ppm of 2-
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15 chlorothioxanthone (22) and 9 % of fumed silica was used; about 2 min of exposure was required to
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18 obtain completely tack-free resin. Finally, they demonstrated that (Cp)trimethylplatinum (62) based
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21 compositions show good adhesion (2 – 4 N/100 mm) to polycarbonate and polybutylene
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24 terephthalate and can be used as sealants for connector plugs and sockets³⁸.
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29 Besides, Wacker Chemie AG demonstrated that coating of connectors plugs can be accelerated by
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32 preheating photocurable formulations with (methyl-Cp)trimethylplatinum (63) to 100 – 125 °C before
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35 application³⁹. Such treatment decreases the viscosity of the formulation, allowing better spreading on
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37
38 the surface of the plugs. They also suggested to use vinyl-functionalized MQ resin instead of silica
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41 to obtain transparent materials⁴⁰. Shin-Etsu Chemical Co., Ltd. showed that (methyl-
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44 Cp)trimethylplatinum (63)-based formulations could be kept in the dark at 40 °C for a month without
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47 thickening⁴¹. After this prolonged storage, the catalyst could still be activated by UV light (50 sec,
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50 100 mW/cm²) leading to complete curing in 1 h at 25 °C
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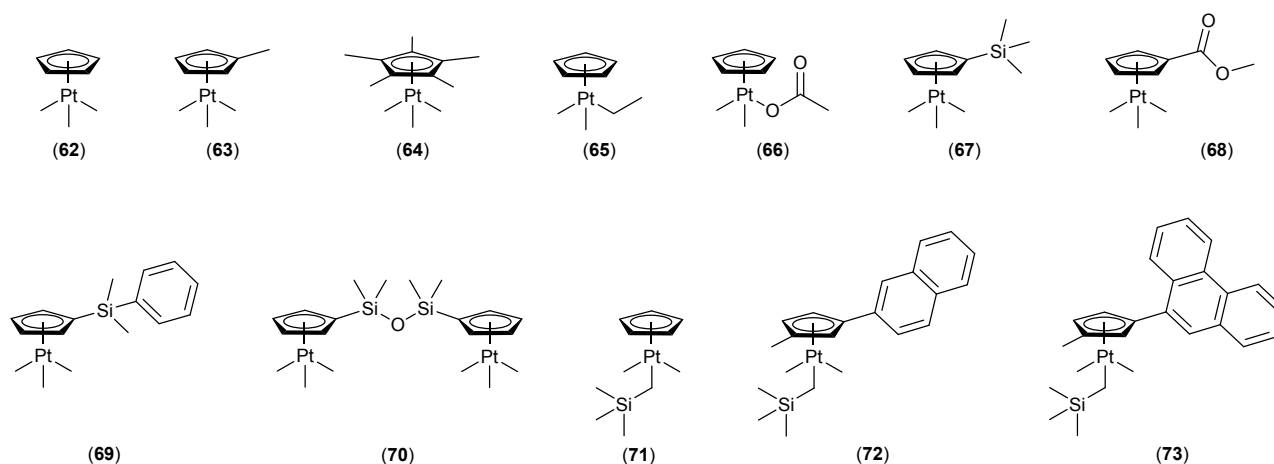


Figure 9. Cyclopentadienyl-based Pt complexes employed as photocatalysts for silicone hydrosilylation curing in cited works.

3.2. Academic works.

(Methyl-Cp)trimethylplatinum (63)/2-chlorothioxanthone (22) initiating system was recently studied in academia by Marchi *et al.*². The reaction between divinyl-PDMS (1) and poly(methylhydrogenosiloxane) (15) (equimolar amounts of vinyl and Si-H groups) under UV and visible lights in the presence of 1000 ppm of (methyl-Cp)trimethylplatinum (63) (corresponding to 610 ppm of Pt content) was studied. First, they tested some concentrations of 2-chlorothioxanthone (22) between 500 and 4000 ppm (Figure 10a) and found that the highest concentration increased Si-H conversion at the beginning of the reaction, but in all cases the conversion could hardly reach 55 % even after 400 sec of exposure to visible light (Astralis 5 gun lamp by Ivoclar Vivadent, intensity 500 mW/cm², wavelength 380 – 515 nm). A blank experiment without photosensitizer showed that the catalyst alone is not active under this type of light, while exposure of this formulation to UV light

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2 resulted in relatively quick Si-H conversion (80 % in about 150 sec). Also, dark-curing was studied
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5 after 10, 30 and 60 sec of visible light exposure (1000 ppm of the catalyst and 4000 ppm of the
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8 sensitizer) (Figure 10b). After 10 sec of exposure, the conversion increased from 5 to 30 % during 1
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11 hour of dark-curing, indicating that the catalyst remained active for long time. Dark curing after 30
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14 or 60 sec of exposure had very similar kinetics and reached about 60 % of conversion in 1 h.
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19 To evaluate the maximum cure depth attainable, the surface of a thick layer of the same formulation
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21 was exposed to visible light for 2 or 4 min and, after 10 min of dark-curing, samples of 0.9 and 1.4 cm
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23 thicknesses, respectively, were characterized. Unfortunately, the authors did not explain whether full
24
25 curing occurred by light penetration or by diffusion of activated catalyst. Thermogravimetric analysis
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27 (TGA) of the samples obtained under UV and visible lights showed similar decomposition profile
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29 with main degradation starting at about 300 °C and resulting to about 70 % of residue at 800 °C. Such
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31 high residue value is quite surprising in the absence of silica. It may be partly explained by two main
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33 factors: i) the ability of (methyl-Cp)trimethylplatinum (**63**) to catalyze the formation of heat-resistant
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35 inorganic substance (ceramization) from silicone at high temperature, similarly to Karstedt's
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37 catalyst⁴³; ii) the generation of a dense crosslinked network coherent with the high functionality of
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39 poly(methylhydrogenosiloxane) (**15**), compared to poly(dimethylsiloxane-co-
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41 methylhydrogenosiloxane) (**2**) that is generally used in commercial hydrosilylation formulations.
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60 Dynamic mechanical analysis (DMA) showed T_g values of -102 and -96 °C for the sample obtained

under visible and UV lights, respectively. These values are much higher than T_g of commonly used PDMS elastomers ($\sim 120^\circ\text{C}$), which a priori confirms the very high crosslink density of the network.

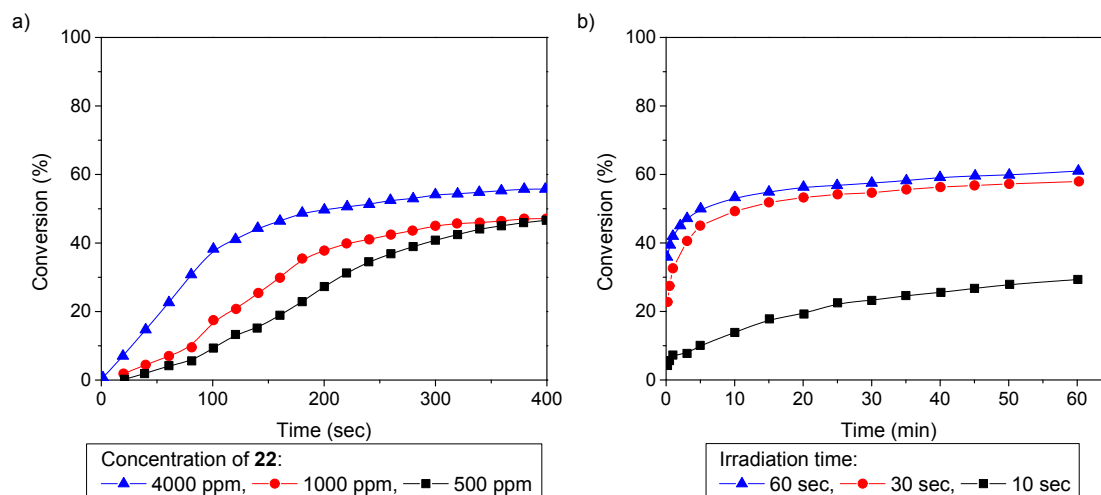


Figure 10. Si-H conversion for different amounts of 2-chlorothioxanthone (**22**) as a photosensitizer in visible light (380 – 515 nm) (a) and evolution of dark-curing after different irradiation time (b) (Catalyst: 1000 ppm of (methyl-Cp)trimethylplatinum (**63**))⁴².

Recently, Xiang *et al.* studied the influence of several other photosensitizers on photohydrosilylation in the presence of the same catalyst (**63**) in order to decrease the required Pt concentration⁴⁴. First, they studied the reaction between divinyl-PDMS (**1**) and poly(methylhydrogenosiloxane) (**15**) under UV light (365 nm LED, 33 mW/cm²) at different catalyst concentrations (50 – 400 ppm, corresponding to 30 – 245 ppm of Pt content). It was found that, in these conditions, 400 ppm of the Pt complex is required to reach Si-H conversion close to 100 % in 300 sec. At 50 ppm of catalyst concentration, conversion did not exceed 50 % after the same time of exposure. Based on these results, the authors chose 100 ppm as a catalyst content to study the

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2 influence of various photosensitizers (33 – 39, Figure 6). Figure 11 shows the Si-H conversion in the
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5 presence of different concentrations of the sensitizers after 100 sec of exposure (we specifically
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8 selected this reaction time to clearly show the influence of the sensitizer on polymerization kinetics,
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11 all things being equal). It could be seen that some compounds (pyrene (33), naphthalene (35), fluorene
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14 (37) and phenanthrene (39)) accelerated hydrosilylation up to a certain concentration, but adding
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17 more of these compounds had the reverse effect and slowed down the reaction. The other three studied
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20 compounds (perylene (34), anthracene (36) and biphenyl (38)) decreased the reaction rate even at the
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23 lowest tested concentration. The authors did not provide clear explanation of the different influence
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26 of these molecules, but as naphthalene showed more pronounced accelerating effect, it was selected
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29 as the most suitable sensitizer for UV-activated hydrosilylation. The cured samples obtained with and
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32 without this photosensitizer were analyzed by tensile test, DMA and TGA. It was found that the
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35 presence of naphthalene during curing resulted in higher values of stress and elongation at break,
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38 higher T_g and larger solid residue at 800 °C (Table 1). This difference in properties was explained by
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41 higher conversion of naphthalene-assisted reaction and consequently higher crosslinking density.
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44 Finally, the example of photolithography using one of the developed resins was demonstrated (Figure
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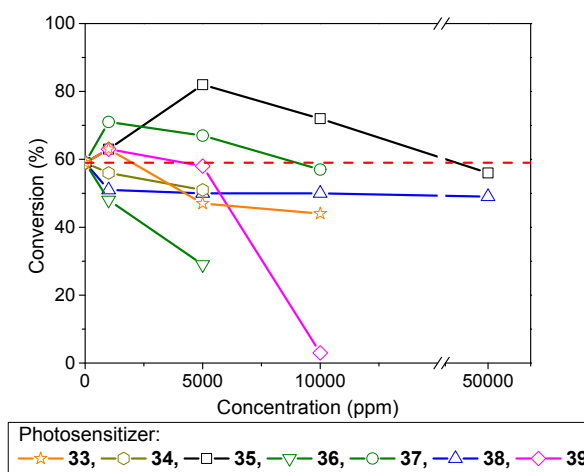
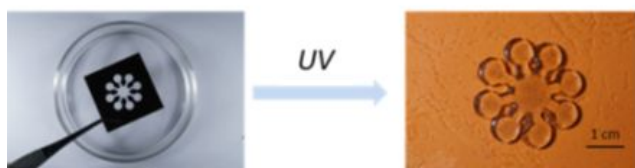


Figure 11. Si-H conversion after 100 sec of UV-activated (365 nm) hydrosilylation vs concentration of photosensitizers (see Figure 6 for the structures)⁴⁴. Lines are only guides for the eyes. The red dotted line corresponds to Si-H conversion without any photosensitizer.

Table 1. Mechanical and thermal properties of photocured silicones described in⁴⁴.

Property	Catalytic system (Methyl-Cp)trimethylplatinum (63)	(Methyl-Cp)trimethylplatinum(63)/ Naphthalene(35)
Elongation at break (%)	248	333
Stress at break (MPa)	0.17	0.23
T _g (°C)	-121	-115
Residue at 800 °C (%)	67.6	72.4



1
2 **Figure 12.** Example of hydrosilylation photolithography process using UV light ⁴⁴. Reproduced with
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5 permission from John Wiley and Sons Inc., Copyright, 2019.
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9 *3.3. New platinum chemistry.*

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13 The GE Company raised an issue about the bad compatibility of such photosensitizers as
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15 anthracene-based ones and suggested a synthesis of cyclopentadienyl-based Pt-complexes containing
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17 chromophore groups (Figure 13)⁴⁵. To study the efficiency of these new complexes, divinyl-PDMS
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19 (1), Si-H containing silicone (SL6020 from GE Silicone Product Division) and the new Pt catalysts
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21 were cured using an RPC UV processor, PPG model 1202, which was fitted with 400 – 500 W
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23 mercury arc lamps, at a line speed of 50 – 100 cm/sec (layer thickness: 0.013 to 0.13 mm). For
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25 comparison, in case of (methyl-Cp)trimethylplatinum(63)-catalyzed reaction, it was required
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27 200 ppm of Pt and 1800 ppm of phenanthrene (39) to reach a non-smear state at a line speed of
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29 50 cm/sec and using a 400 W lamp. Whereas, synthesized [1-methyl-3-(9'-phenanthryl)-
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31 cyclopentadienyl] trimethylplatinum (74) solely achieved non-smear coating at a line speed of
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33 100 cm/sec with a 400 W lamp, using only 100 ppm of Pt. Also, the inventors estimated the shelf life
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35 of the formulations (100 ppm of Pt) by measuring the time required in the absence of light to show a
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37 viscosity increase sufficient to interfere with free flow when shaken. This time was 24 – 48 h for
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39 (methyl-Cp)trimethylplatinum(63)-based formulation, against 96 – 144 h for new synthesized
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41 complexes (74 – 76).
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The GE Company also reported the synthesis of silicon-containing platinum complexes (**71** – **73**, Figure 9) and tested them as catalysts for photohydroxylation⁴⁶. First, they showed that the bath life (time of “viscosity increase sufficient to interfere with free flow when shaken”) of the formulations containing divinyl-PDMS (**1**), poly(dimethylsiloxane-co-methylhydrogenosiloxane) (**2**) and complexes **72** or **73** (96 h) was longer than the formulation with (methyl-Cp)trimethylplatinum (**63**) (24 – 48 h). The formulations with complexes **71** and **72** were used to treat Kraft paper under an exposition to a fluorescent light source. 1 h was required to obtain tack-free paper treated with the formulation of **71** and ‘only’ 26 min for the formulation with **72**. Both catalysts were more active in these conditions than (methyl-Cp)trimethylplatinum (**63**) that required > 24 h.

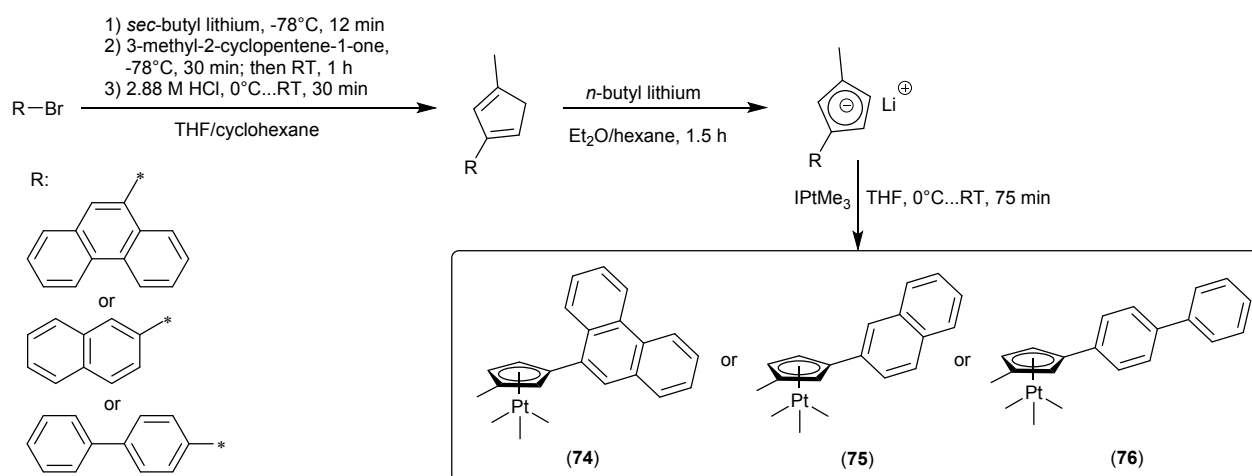


Figure 13. Scheme of the synthesis of Pt complexes containing a photosensitizing group⁴⁵.

Another modification of cyclopentadienyl-based Pt catalyst was patented by Wacker Chemie AG⁴⁷. To decrease the volatility of Pt-catalyst that can be a problem during vacuum treatment of the formulation, the inventor suggested a synthesis of platinum complexes containing hydrolysable silyl

groups (**77** – **80**) for subsequent co-hydrolysis with dihydroxy-PDMS (**16**) (Figure 14). The obtained catalysts were tested in hydrosilylation crosslinking and demonstrated slightly higher activity under UV light (230 – 400 nm, 70 mW/cm²) than (methyl-Cp)trimethylplatinum (**63**).

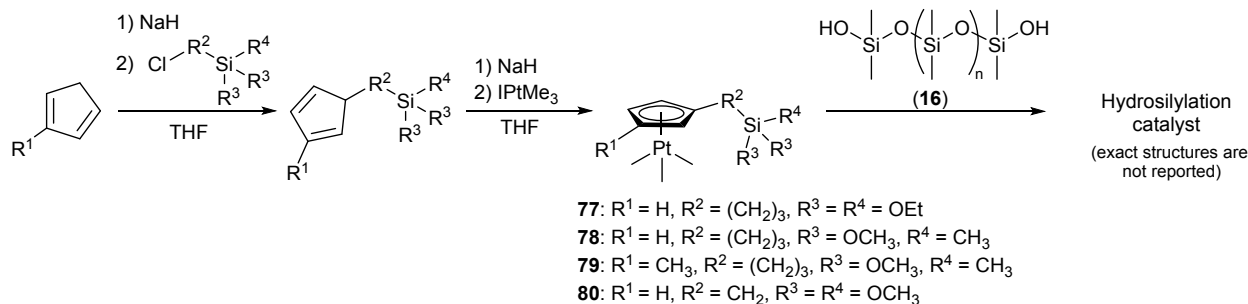
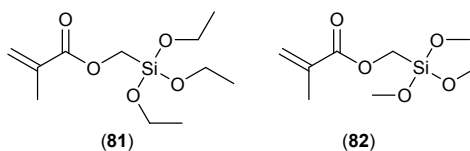


Figure 14. Synthesis of hydrosilylation catalyst linked to polymer chain reported by Wacker Chemie AG⁴⁷.

3.4. Application of (methyl-Cp)trimethylplatinum (**63**)-based formulations.

Momentive Performance Materials GmbH disclosed the use of (methyl-Cp)trimethylplatinum (**63**)-based formulations for production of thick-walled silicone molding products or of thick-walled silicone coatings⁴⁸. (XA) Flash lamp (xenon) (Blassing, Essen) (emission power of 34.9 J/individual flash at 12.5 Hz) was employed to conduct photo-hydrosilylation of the silicone oils filled (or not) with silica to obtain objects of up to 50 mm in thickness. The obtained materials had hardness between 20 and 60 Shore A depending on the formulation. One of the obtained samples was subjected to tensile test, giving an elongation at break of 670% and a tensile strength of 4.8 MPa. This work was followed by a patent application of Wacker Chemie AG⁴⁹ where they suggested similar formulations

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2 with the same catalyst (**63**), but they used only short UV irradiation (1 sec) to fix the shape of the
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5 resin and thermal curing at 140 °C (5 min) afterwards. The inventors explained that this method
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7 improved the adhesion of the silicone to the support material. Also, it was demonstrated that adhesion
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9 of such compositions to polybutylene terephthalate and polyamide could be improved by addition of
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12 alkoxy silanes, namely (triethoxysilyl)methyl methacrylate (**81**) or (trimethoxysilyl)methyl
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15 methacrylate (**82**) (Figure 15)⁵⁰.



29 **Figure 15.** Adhesion promoters employed by Wacker Chemie AG⁵⁰.

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32 Interestingly, (methyl-Cp)trimethylplatinum (**63**) was quite widely employed in silicone
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34 formulations to produce transparent silicone resins that can be used in optical devices; solely in the
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36 year 2021, five patent applications were published⁵¹⁻⁵⁵. Also, the same catalyst was applied to light-
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38 emitting-diode (LED) encapsulating materials⁵⁶⁻⁵⁸, in the latter case using a very low content of
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40 (methyl-Cp)-trimethylplatinum (**63**) (5 ppm)⁵⁸. To do so, Shin-Etsu Chemical Co., Ltd. used
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42 photocuring only to fix the shape of the deposited resin before thermal curing, similarly to previously-
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44 mentioned Wacker's patent⁴⁹. The same company reported the use of zeolite as a filler for such
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46 photoactive formulations⁵⁹: the mixture containing 60 wt% of high silica zeolite HiSiv 3000 was
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1
2 cured by a UV beam of 5 J/cm² to obtain a material with a hardness of 50 Shore A. It was also shown
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5 that thermal post-curing for 2 h at 200 °C could increase the hardness to 75 Shore A.
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9 **4. Photohydrosilylation with Pt β -diketonates complexes.**

10 *4.1. Pt bis(β -diketonates)*

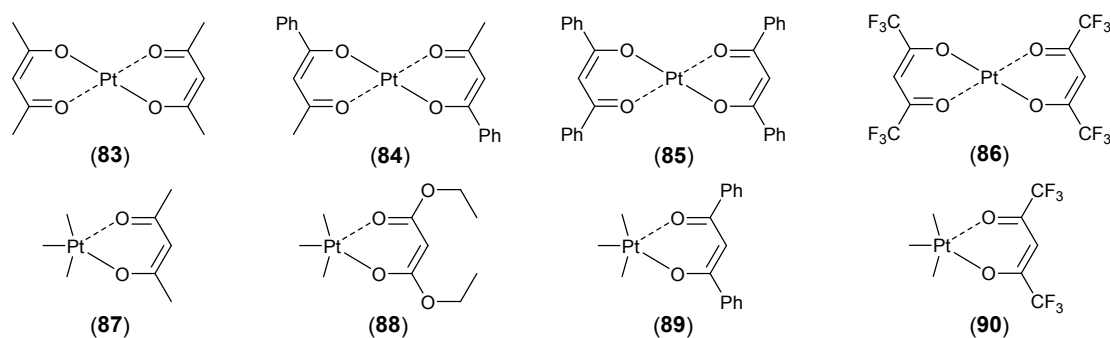
11
12
13 The 3M Company reported in the nineties another type of photoactive catalyst (Pt(II) β -diketonates)
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15 for silicone hydrosilylation reaction^{60,61}. Pt(II) acetylacetonate (Pt(acac)₂) (**83**) and its derivatives (**84**
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17 - **86**) (Figure 16) were suggested as catalysts for photohydrosilylation and they were compared to
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19 (Cp)trimethylplatinum (**62**) and (phenyldimethylsilyl-Cp)-trimethylplatinum (**69**) (see Figure 9). The
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21 formulations containing divinyl-PDMS (**1**), poly(methylhydrogenosiloxane) (**15**) and various Pt-
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23 complexes were tested for photo-curing under visible light source (“Visilux” 2 dental curing light,
24
25 (Cp)trimethylplatinum (**62**) and (phenyldimethylsilyl-Cp)-trimethylplatinum (**69**) (see Figure 9). The
26
27 formulations containing divinyl-PDMS (**1**), poly(methylhydrogenosiloxane) (**15**) and various Pt-
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29 complexes were tested for photo-curing under visible light source (“Visilux” 2 dental curing light,
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31 wavelength 400 – 500 nm). It was found that 50 ppm was the optimal Pt concentration in case of
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33 Pt(acac)₂ (**83**); tack-free polymer could be obtained after 37 sec of exposure, while an increase of the
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35 catalyst concentration up to 1000 ppm did not lead to faster curing (for the record, an increase of
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37 concentration of cyclopentadienyl-containing complexes resulted in faster curing up to 1000 ppm of
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39 Pt content^{60,61}). In the presence of 50 ppm of Pt in the form of Pt(acac)₂ (**83**), cure depth could reach
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41 6 cm after 120 sec of exposure. Photocuring with other β -diketonate complexes was performed under
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43 similar conditions; Pt(II) benzoylacetonate (**84**) had very similar activity to Pt(acac)₂ (**83**), but the
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45 other two catalysts (**85**, **86**) were less active and required about 2 times longer exposure to obtain
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1
2 tack-free polymer. Also the formulations with Pt(acac)₂ (**83**) were tested under “Caulk-Hanovia” UV-
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5 light with maximum output at 366 nm. The catalyst was active in these conditions, but almost 6 times
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8 longer exposure was required than under the visible light. This result is surprising knowing that this
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11 catalyst absorbs well in UV region⁶²; unfortunately, in the patent⁶⁰, there is no information about the
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14 power of UV and visible light sources, which could explain the slower curing under UV light. The
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17 authors then present thorough tests of self-stability of described formulations at 4, 25 and 50 °C. It
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20 was found that Pt(acac)₂ (**83**) leads to more stable formulations than (Cp)trimethylplatinum (**62**). For
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23 instance, Pt(acac)₂ (**83**) formulation with 200 ppm of Pt content remained fluid for 24 – 48 hours at
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26 50 °C and more than 150 days at room temperature. The formulations with 990 ppm of Pt were stable
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29 at 4 and 25 °C for more than 200 days. Finally, they showed few examples of applications of such
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32 formulations with addition of up to 7.5% of fumed silica to produce silicone gaskets or a tyodont
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45 Shin-Etsu Chemical Co., Ltd. also demonstrated that hydrosilylation formulation containing
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48 Pt(acac)₂ (**83**) (5 ppm of platinum content) could be kept for 1 month at 40 °C and that the catalyst
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51 could be subsequently activated by UV light (50 sec, 100 mW/cm²) resulting in complete cure in
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54 1 hour⁴¹.

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57 In an article, Sangermano *et al.* studied photohydrosilylation silicone curing catalyzed by Pt(acac)₂
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60 (**83**) under UV-light (medium pressure mercury lamp (Italaquartz, Milano), 50 mW/cm²)⁶³. In contrast

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2 to above described patent⁶⁰, they worked with much higher catalyst concentrations (500 or 1000 ppm
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6 corresponding to 250 and 500 ppm of Pt content, respectively) and longer exposure time (5 min).
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9 500 ppm of catalyst concentration was selected as an optimal one, because a higher concentration did
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12 not accelerate the curing (Figure 17a), and it was claimed that at lower catalyst content, it was not
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14
15 possible to obtain a fully cured tack-free sample. Layers of different thicknesses (1, 2, 3 and 4 cm)
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18 were cured for 5 min under a UV light, even the thickest sample cured full-depth. Nevertheless, IR
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21 analysis of the bottom side of the samples showed the presence of unreacted Si-H groups that
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26 increased with the depth of the sample.



41 **Figure 16.** Pt β -diketonates employed in reviewed works as photoactive catalyst of silicone
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45 hydrosilylation curing.

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49 Besides, dark curing after short UV-irradiation was studied; it was found that after 10, 30 or 60 sec,
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52 the conversion of Si-H groups continued to increase for at least one hour (from 7, 20 and 40 % to 40,
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55 43 and 60 %, respectively) (Figure 17b). The authors explain this dark curing as well as deep curing
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59 by the formation of less active colloidal platinum, however it is not clear how they came to this
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conclusion. The question of deep and dark curing was addressed in more details in a following paper of the same authors⁶⁴. They found out that in these conditions (500 ppm of Pt(acac)₂, 50 mW/cm²), curing can proceed via a thermal-frontal mechanism: the UV light activates the catalyst on the surface of the sample and the heat released by exothermal hydrosilylation generates a thermal front with the activation of the catalyst in the deeper layers of the formulations. A temperature of up to 85 °C was detected on the depth of 1 cm from the surface.

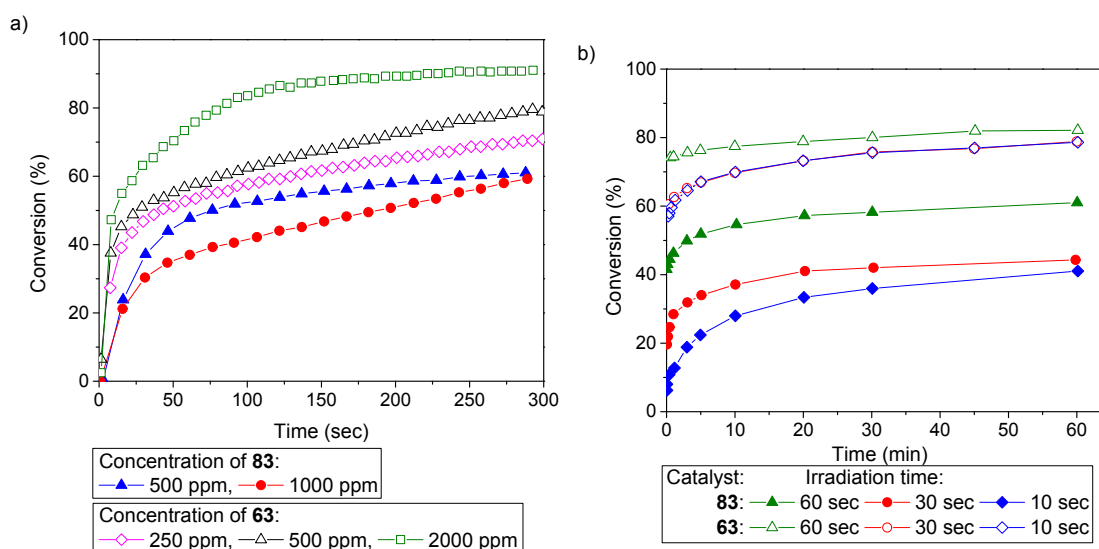


Figure 17. Si-H conversion for different amounts of Pt(acac)₂ (**83**)⁶³ and (methyl-Cp)trimethylplatinum (**63**)⁶⁵ under UV light (a) and evolution of dark-curing after different irradiation time (500 ppm of Pt(acac)₂ (**83**)⁶³ or 1000 ppm of (methyl-Cp)trimethylplatinum (**63**)⁶⁵) (b).

In the next work of the same research group, the authors compared the activity of Pt(acac)₂ (**83**) to (methyl-Cp)trimethylplatinum (**63**) as catalysts of UV-activated hydrosilylation⁶⁵. It was shown that even in the presence of a 'low' concentration (250 ppm) of (methyl-Cp)trimethylplatinum (**63**),

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2 hydrosilylation occurs at higher rate than in the presence of Pt(acac)₂ (**83**) (500 ppm) (Figure 17a).
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5 Moreover, the reaction can be accelerated by increasing (methyl-Cp)trimethylplatinum (**63**) content
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8 to 500 or 2000 ppm (Figure 17a). It was shown that dark curing as well as thermal front reaction
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10 occurred for each catalyst, but Cp-containing complex resulted in higher conversion during shot
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12 exposure, leading to smaller conversion change in the dark (from 58 to 80% after 10 sec with
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15 1000 ppm of (methyl-Cp)trimethylplatinum (**63**)) (Figure 17b).
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22 One more article compares this UV-activated process to thermal hydrosilylation in the presence of
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24 Pt(acac)₂ (**83**)⁶⁶. The thermally-induced reaction was much slower and required 3 h at 150 °C to reach
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26 83% of conversion in comparison to less than 5 min under UV-light. TGA of thermally and photo-
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28 cured samples showed that they had similar stability with main decomposition around 400 °C, but,
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30 more interestingly, the final residue at 800 °C was around 20 – 30 % for both samples, indicating that
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32 this catalyst did not (or not efficiently) catalyze ceramization of silicone at high temperature, in
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34 contrast to Cp-based system described above (Section 3.2)^{42,44}. To complete the picture, it is worth
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36 mentioning that in 1993, Yang developed a method to follow the reaction of photohydrosilylation by
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38 IR spectroscopy⁶⁷ and this (or similar) method was employed by Sangermano's team in reviewed-
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40 above works, but the catalyst used in this work was not mentioned.
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55 Quite recently, a full study describing simple molecules engaged in photohydrosilylation with
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57 Pt(acac)₂ (**83**) under UV-light (Dymax UV curing chamber with a UV bulb part number of 38560,
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2 wavelength from 380 nm to visible light, intensity 350 mJ/cm²) was reported in a patent published by
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5 Dow Corning Corporation (Table 2)⁶⁸. An interesting finding is that reactive groups in vinyl-based
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8 molecules must be separated by at least 4 atoms, otherwise, the molecules with close positions of
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10 vinyl-groups require extended exposure time or do not cure (Examples 1, 2, 3 and 8 in Table 2). This
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12 phenomenon was explained in the patent by “undesirable complexing with the photoactivated
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14 hydrosilylation catalyst”. Apart from this, there is no explanation of the choice of the reagents. It can
15
16 be noticed that the inventors used several low-molecular compounds, one linear oligomer as H-Si
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18 reactant (Examples 8 – 15 in Table 2) and one branched oligomer as vinyl reactant (Example 4 in
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20 Table 2). It is worth noting that in some cases the curing required less than 10 sec (Examples 4, 7, 12
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22 – 15 in Table 2) and in certain examples even at low concentration of catalyst (Examples 14, 15 in
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24 Table 2). The formulations 13 and 15 from the Table 2, were also reprocessed by adding silica
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26 (diameter of 50 μm) and 2 cm thick layers were subjected to 9 sec of UV-exposure followed by 10 sec
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28 delay, after which the entire thickness of the samples was solidified. Unfortunately, exact
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30 compositions of these formulations are not clear; for the first one the silica content is declared to be
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32 70%, which is much higher than commonly used values, whereas silica content in the second one was
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34 not mentioned at all.
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56 Table 2. Pt(acac)₂-based formulations and their curing time as described in⁶⁸.
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H-Si Reactant ^a	Vinyl Reactant ^a	[Vi]/[SiH]	Pt (ppm)	Curing time ^b (sec)
1	94	1	20	no cure
2	92	1	20	no cure
3	95	1	200	290
4	91	0.33	200	7
5	1 (n = 4.5)	2.3	100	10
6	1 (n = 4.5)	1.7	200	10
7	93	1	200	5
8	92	1	200	120
9	1 (n = 4.5)	0.6	20	87
10	1 (n = 4.5)	0.6	200	37
11	15 (n = 65)	1.6	200	10
12	93	0.5	200	4
13	93	1	200	6
14	93	1	30	8
15	93	1	10	9

^a see figures 2 and 18 for the chemical structures; ^b Exposure time needed for the liquid to solidify.

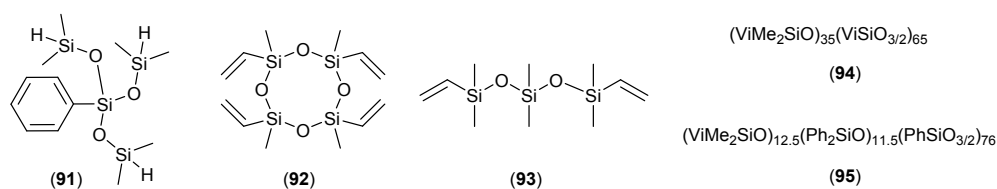


Figure 18. Siloxane molecules and silicone resins employed as monomers in DOW's patent⁶⁸.

4.2. Pt mono(β -diketonates).

Four other platinum complexes with β -diketonate single ligands (**87** – **90**, Figure 16) were synthesized and studied in photohydrosilylation reaction^{69,70}. The kinetics of crosslinking reaction between divinyl-PDMS (**1**) and poly(dimethylsiloxane-co-methylhydrogenosiloxane) (**2**) were studied and activities of the complexes were compared to Pt(acac)₂ (**83**) and (Cp)trimethylplatinum (**62**) (Figure 19). Irradiation was performed using an air-cooled HPK125W medium-pressure mercury lamp whose emission was filtered by a water-containing quartz cell and a Pyrex glass plate (wavelength range not given). It was found that the activity of the complexes with methyl (**87**) and ethoxy (**88**) groups were close to (Cp)trimethylplatinum (**62**), while the other two catalysts (**89**, **90**) were less active and closer to Pt(acac)₂ (**83**).

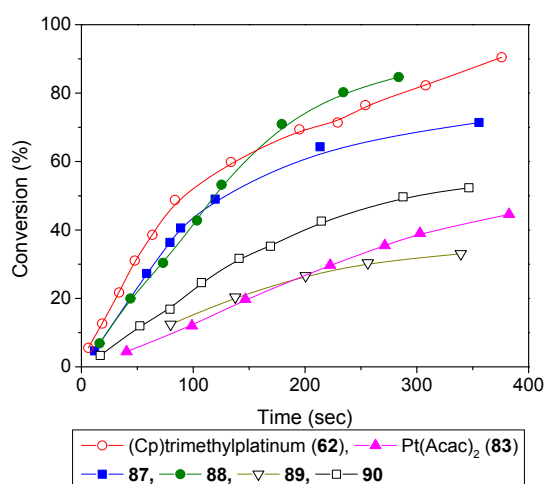


Figure 19. Si-H conversion in photohydrosilylation reaction with different single-ketonate liganded Pt complexes compared to **62** and **83** catalysts (Pt content: 250 – 300 ppm)⁶⁹.

4.3. Applications of Pt β -diketonates formulations.

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2 An interesting application of Pt(acac)₂ (**83**) was patented by Shin-Etsu Chemical Co., Ltd.⁷¹. They
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5 prepared adhesive photocurable compositions to be used in the production of Fresnel lenses with a
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8 glass substrate for concentrator solar power systems. Similarly to the described above systems,
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12 divinyl-PDMS (**1**), bis(trivinylsilyl)-polydimethylsiloxane (**12**), poly(methylhydrogenosiloxane) (**15**)
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15 (see Figures 2 and 5) were used. To promote the adhesion of the resins, one of two alkoxy-containing
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18 siloxanes (**17** or **96**, Figures 5 and 20) was employed. With Pt content around 30 ppm, the curing time
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21 was only 0.8 sec, but most probably this short exposure activated the catalyst that remained active
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24 after the exposure and dark curing took place (hardness was measured after 5 or 48 h). The higher
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27 crosslinking speed in comparison to previously described Pt(acac)₂-based system⁶⁰ can be explained
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30 either by the reactivity of used components or by the employed UV source. Here the authors did not
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33 provide the wavelength of the UV radiation nor the commercial name of the lamp, only intensity of
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36 250 mW/cm² was reported. The hardness of obtained materials was measured by Type A Durometer
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39 according to JIS K-6253 5 hours and 2 days after curing. The values were between 19 and 52 after 5
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42 hours and increased to 37 – 58 after 2 days.
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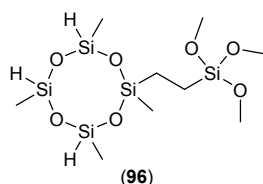


Figure 20. Alkoxy-containing siloxane employed as an adhesion promoter by Shin-Etsu⁷¹.

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2 Recently, it was demonstrated that that Pt(acac)₂ (**83**)-based silicone composition can be filled with
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6 zeolite to obtain ethylene absorbing material,⁷² while filling with aluminum powder allowed to obtain
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9 thermally conductive grease^{73–75.a}. Similarly to (methyl-Cp)trimethylplatinum (**63**) the catalysts **83**
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11
12 and **86** found applications in silicone formulations used for encapsulating LEDs^{57,76,77}.

15 16 **5. Pt-catalyzed hydrosilylation in the presence of radical photoinitiators.**

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19 In contrast to the described above systems using photoactive catalyst, the GE Company disclosed
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21
22 a method to cure silicone by hydrosilylation under UV-light using a free-radical-type photoinitiator
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25 and a Pt-based catalyst generally used in thermally-activated hydrosilylation⁷⁸. The inventor explains
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28 that the radical photoinitiator first crosslink the surface and then Pt catalyst allows finishing the
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31 hydrosilylation at room or hot temperature. Polysiloxane chains containing methyl-hydrogenosiloxy,
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34 methyl-vinylsiloxy, and dimethylsiloxy units were cured in the presence of “platinum-octyl alcohol
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37 complex” (Pt content 2 – 3 ppm) as hydrosilylation catalyst, 4.5 % of *t*-butylperbenzoate (**5**) (Figure
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conveyor of PPG Model QC 1202 AN Processor (neither the structure of PDMS nor platinum

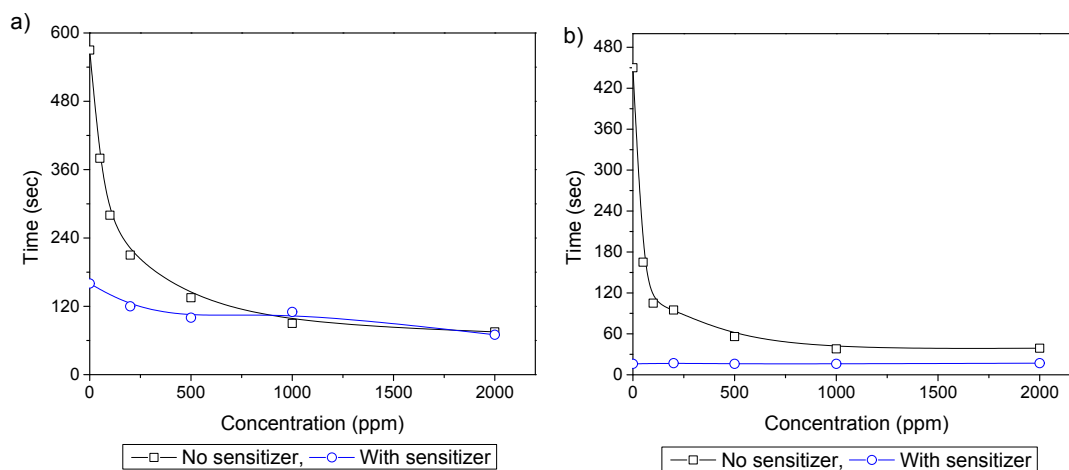
^a The word “grease” used in these patents refers to a matter that is not a lubricant. It is placed between fixed heat-generating part and a heat-dissipating part, as a thermal conductive paste. Crosslinking helps to retain the shape of this layer. Probably, “thermally conductive paste” would be a more appropriate term here, but “thermal grease” is the terminology used in patents.

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2 complex were reported). It was found that a layer thickness of up to 0.1 mm could be completely
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5 cured at a UV lamp power of 400 W and conveyor line speed of up to 50 cm/sec. UV exposure of a
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8 thicker layer (0.2 mm) resulted in “soft” cure or, in other words, a cure confined to the surface, but
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12 after 17 hours at room temperature, the sample was completely cured. This result can be compared to
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15 the one described above (Section 3.3) and more recently patented system with Cp-based photoactive
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18 catalyst (**74**)⁴⁵: much higher Pt-content (100 ppm) was required under the same UV exposure even if
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21 newly synthesized catalyst (**74**) allowed to double the conveyor line speed (100 cm/sec).
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26 Whereas the GE Company used radical photoinitiators to activate an otherwise non-photoactive
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28 system, the 3M Company applied radical initiators to accelerate an already-photoactive systems³¹.
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32 The catalytic activity of four of COD-Pt complexes (di(4-methylphenyl)-Pt(COD) (**42**), di(4-
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34 trifluoromethylphenyl)-Pt(COD) (**51**), di(4-methoxyphenyl)-Pt(COD) (**53**) and di(4-
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36 trimethylsilylphenyl)-Pt(COD)) (**58**) (Figure 7) (200 ppm Pt content) in the presence of radical
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38 photoinitiators (**6 – 9**, Figure 4) was studied. In contrast to the sensitizer study²⁹, all tested radical
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41 initiators (apart from one exception: di(4-trimethylsilylphenyl)-Pt(COD)) (**58**) with Darocur 1173 (**7**)
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43 under visible light) accelerated the curing with all four catalysts under UV (“black” light, 365 nm)
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46 and visible light (“Visilux” 2 dental curing light, 400 – 500 nm) systems. Irgacure 651 (**8**) was the
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49 most effective whatever the considered catalyst. The influence of its concentration in curing was
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52 studied in an example with di(4-methoxyphenyl)-Pt(COD) (**53**) catalyst (Figure 21). It was found that
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2 under UV light, required cure time decreased when Irgacure 651 (**8**) content was increased at least to
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5 2000 ppm (Figure 21a), but under visible light the minimum cure time was at 1000 ppm, and further
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8 increase of **8** concentration did not influence the reaction time (Figure 21b). Also, the influence of
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11 Irgacure 651 (**8**) was studied in the presence of a photosensitizer (2-chlorothioxanthone) (**22**) (Figure
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16 21). Interestingly, in this case, Irgacure 651 (**8**) did not influence so drastically the cure time under
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19 UV-light and did not accelerate the reaction under visible light at all. The inventors did not explain
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22 such findings, nor did they provide any evidence that it acts as a radical initiator as well. It could be
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24
25 suggested that in these conditions, the aromatic ketones play the role of photosensitizers (as in the
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28 patent²⁷, see section 3a and 3b) so that in the presence of a more active sensitizer, its contribution is
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32 less noticeable.



51
52 **Figure 21.** Influence of Irgacure 651 (**8**) concentration on the required cure time without and with
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55 1000 ppm of 2-chlorothioxanthone (**22**) as a photosensitizer under UV (a) and visible (b) light³¹.

The 3M Company also tested the influence of radical photoinitiators on silicone hydrosilylation curing catalyzed by (methyl-Cp)trimethylplatinum (**63**)⁷⁹. They tested Irgacure 651 (**8**), Irgacure 184 (**6**), Darocur 1173 (**7**), Darocur 1116 (**9**) in the presence of 960 ppm of Pt-catalyst and found that all tested compounds accelerated the curing. Darocur 1173 (**7**) was selected to study the influence of its concentration on cure time with and without a photosensitizer (**22**) (Figure 22). It did not accelerate the curing, except under UV-light at low concentration in the absence of sensitizer. Same as in previously described system³¹, the role of the added aromatic ketones was not explained.

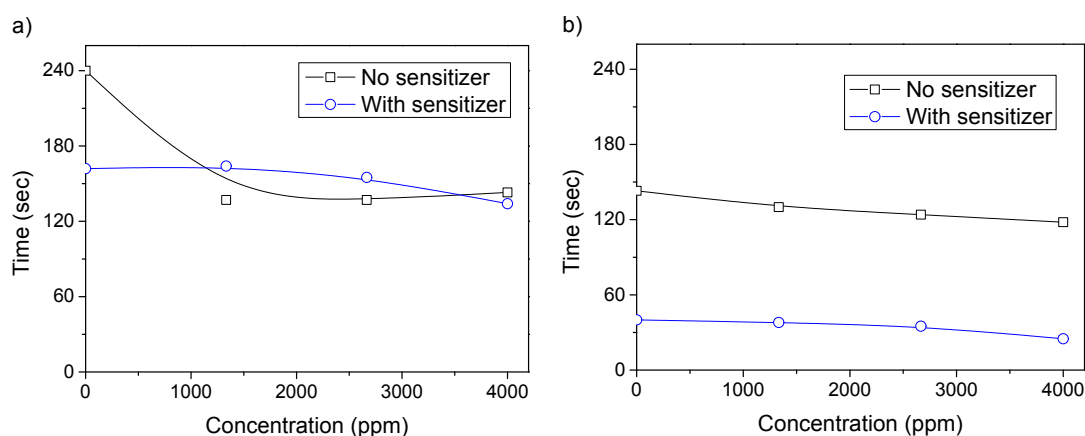


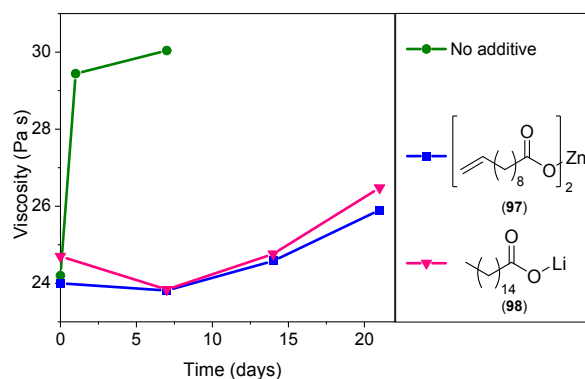
Figure 22. Influence of Darocur 1173 (**7**) concentration on the required cure time without and with 1000 ppm of 2-chlorothioxanthone (**22**) as a photosensitizer under UV (a) and visible (b) light⁷⁹.

6. Increase of shelf life of photoactive hydrosilylation formulations.

6.1. Photoactive formulations without inhibitor.

While studying the stability of photohydrosilylation mixtures, researchers from Wacker Chemie AG found out that silicone formulations for hydrosilylation might contain strong protic acid

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2 impurities ($pK_a < 2.5$) coming from PDMS synthesis (acidic catalyst is used) or from fumed silica
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6 (chlorosilanes generate hydrogen chloride).⁸⁰ In the patent, it was demonstrated, using model
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9 compounds, that after the removal of this trace amount (1 – 10 ppm) of strong protic acids by thorough
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12 purification, the stability of hydrosilylation formulation increased. Complete removal of traces of
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15 strong acids may be too difficult in case of polymeric formulations; as a simpler solution, it was
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18 shown that some salts of fatty acids (**97**, **98**, Figure 23) can trap free protons and improve the stability
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21 of (methyl-Cp)trimethylplatinum (**63**)-based photohydrosilylation compositions (Figure 23). More
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24 importantly, the formulations with such additives could be crosslinked by UV light (exact conditions
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26 were not provided) after 8 weeks of storage, while the base composition could not be completely
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29 cured by means of UV irradiation after 7 days of storage.



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50 **Figure 23.** Evolution of viscosity of hydrosilylation formulations in the presence of (methyl-
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52 Cp)trimethylplatinum (**63**) (15 ppm of Pt content) and zinc undecylenate (**97**) (141 ppm) or lithium
53
54 palmitate (**98**) (282 ppm)⁸⁰.

1
2 Three Bond Company suggested using isocyanide “inhibitors” (**99** – **104**, Figure 24a) to improve
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4
5 the shelf life of Pt-catalyzed photocuring silicones⁸¹. They described the synthesis procedure to
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9 introduce these isocyanide molecules into new complexes and test them in photo-curing. The
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12 complexes were synthesized from potassium hexachloroplatinate(IV) (K_2PtCl_6) and one of the
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15 following isocyanides: *t*-butyl isocyanide (**99**), cyclohexyl isocyanide (**100**), phenyl isocyanide (**101**),
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18 benzyl isocyanide (**102**), 4-chloro-phenyl isocyanide (**103**) or 4-methoxy-phenyl isocyanide (**104**).
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22 The complexes were separated from the reaction mixtures, purified by recrystallization from ethanol,
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25 and analyzed by IR spectrometry. Unfortunately, the structures of the obtained catalysts were not
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28 presented. The activity of the synthesized complexes was tested with divinyl-terminated PDMS
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31 (molar mass of 60 kg/mol) and Si-H functionalized oligomers (molar mass of 2000 g/mol) at 30 ppm
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34 of catalyst content. 10 g of each formulation was subjected to 2 J of UV exposure. It was found that
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37 all catalysts are active in these conditions, but only the complexes with aliphatic isocyanides (**99**,
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42 **100**) resulted in materials fully insoluble in toluene. The samples obtained with aromatic ligands (**101**
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45 – **104**) contained from 45 to 75 % of toluene insoluble fraction. The stability of the formulations was
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48 tested at 50 °C and it was found that those containing isocyanides with aliphatic ligands (**99**, **100**) and
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51 with 4-methoxy-phenyl group (**104**) had the longest shelf life (Figure 24b).
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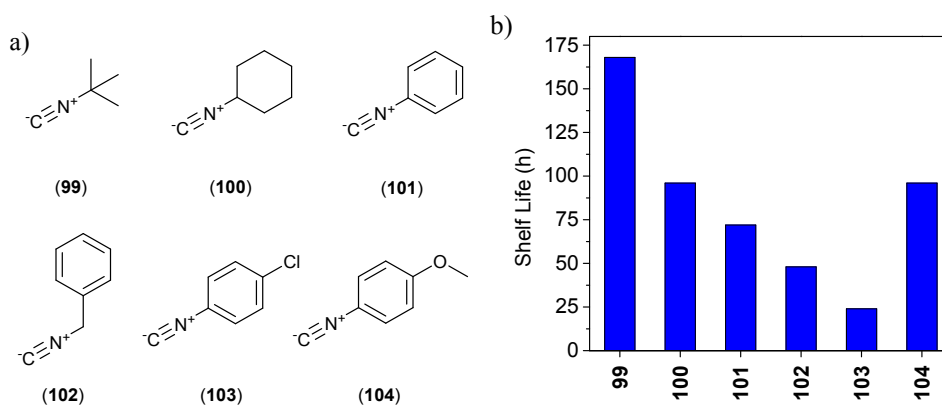


Figure 24. Structures of isocyanides described by Three Bond Company (a) and shelf life of formulations containing these compounds (b).⁸¹

6.2. Photoactive formulations containing an inhibitor.

Shin-Etsu Chemical Co., Ltd. studied hydrosilylation reaction by photoactive catalysts in the presence of inhibitors (**105**, **106**, Figure 25) in order to develop low-crosslink-density silicone gels for damping materials³². The following catalytic systems were employed (catalyst/inhibitor): Pt(acac)₂ (**83**) (400 ppm)/1-ethynylcyclohexanol (**105**) (500 ppm), Pt(acac)₂ (**83**) (400 ppm)/tetramethylethylenediamine (**106**) (8 ppm), Me₂Pt(COD) (**61**) (400 ppm)/ 1-ethynylcyclohexanol (**105**) (500 ppm). The shelf life of these compositions was not studied, but it was demonstrated that without UV light, they did not crosslink after 30 min, even at 120 °C. On the contrary, 400 seconds of UV exposure (100 mW/cm²) was enough to crosslink these formulations. Recently, Elantas Beck GmbH patented similar photohydrosilylation formulations with (methyl-Cp)trimethylplatinum (**63**) (30 ppm) and 1-ethynylcyclohexanol (**105**) or 3,5-dimethyl-1-hexyn-3-ol (**107**) (19 ppm)⁸². Such formulations had a shelf life at room temperature of more than 3 months.

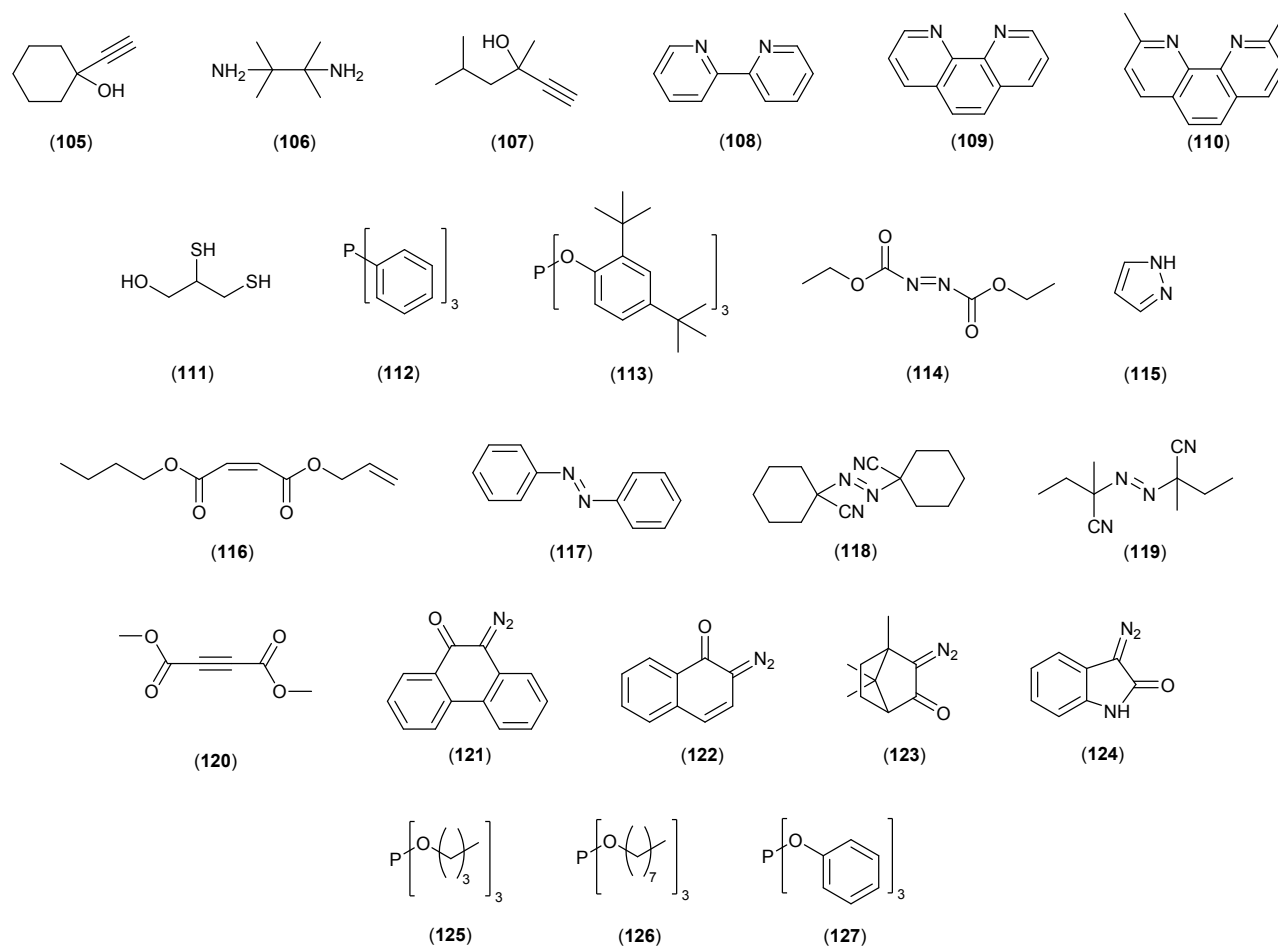


Figure 25. Inhibitors of hydrosilylation employed in photo-curing silicone formulations.

Another attempt to improve the shelf life of photoactive hydrosilylation compositions was published by Wacker Chemie AG⁸³. They suggested using bidentate ligands (108 – 111, Figure 25) with cyclopentadienyl-based Pt complexes as catalysts; unfortunately, the structures of most of them are unclear, because only ambiguous names were provided. The shelf life of studied mixtures was several days without inhibitors and more than 8 months in the presence of bidentate inhibitors (108 – 111). Gelling time of these formulations was determined as the time required to double the dynamic starting viscosity after 10 sec of UV exposure (70 mW/cm²). These values were between 20 and

40 sec for inhibitor-free systems and almost did not change with the addition of the inhibitor. The same company also patented some hydrosilylation formulations containing triphenylphosphine (**112**) or tris(2,4-di-tert-butylphenyl)phosphite (**113**) as inhibitors to increase the shelf life of the mixtures⁸⁴. SiH- and vinyl containing silicone mixture (SEMICOSIL® 912 by Wacker Chemie AG) was mixed with (methyl-Cp)trimethylplatinum (**63**) (30 ppm of Pt content) and the evolution of viscosity was studied with and without inhibitors (Figure 26). In the presence of organophosphorus inhibitors, the viscosity did not evolved significantly after 36 weeks, while inhibitor-free composition crosslinked after 19 weeks. It was shown that such formulations can crosslink in 11 – 13 min after short exposure to UV light (60 sec, 6 mW, 320-500 nm), but photoactivity after prolonged shelf time was not tested.

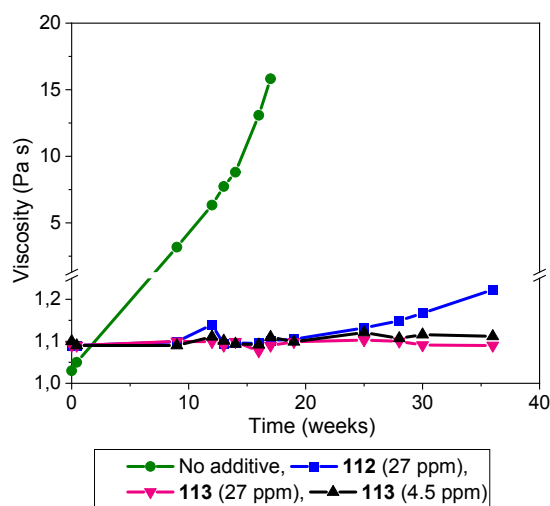


Figure 26. Evolution of viscosity of hydrosilylation formulations in the presence of (methyl-Cp)trimethylplatinum (**63**) and triphenylphosphine (**112**) or tris(2,4-di-tert-butylphenyl)phosphite (**113**)⁸⁴.

6.3. Karstedt's-catalyst-based formulations.

6.3.1. Diethyl azodicarboxylate (DEADC) as a photoactive inhibitor.

As an alternative to photosensitive catalysts, it was proposed that room-temperature active catalyst paired with photosensitive inhibitors could be used to achieve light-induced hydrosilylation. To our knowledge, the first example of such process was reported by the GE Company⁸⁵. They prepared silicone formulations containing 90 ppm of Pt in the form of Karstedt's catalyst and 900 or 1800 ppm of diethyl azodicarboxylate (DEADC, **114**, Figure 25) and studied their photohydrosilylation under UV light (Hanovia medium pressure UV lamp, 300 W/in). It was found that in the presence of 1800 ppm of the inhibitor, 3.15 J/cm² of UV exposure is required to obtain smear-free film on Al-support. At lower inhibitor concentration (900 ppm), the required exposure is reduced to 2.5 J/cm². Also, shelf life was measured for these formulations at 25 °C under "normal room lightning conditions", the value obtained were >6 h and >4 h for 1800 ppm and 900 ppm of DEADC, respectively. Interestingly, benzophenone (**40**, Figure 6) was tested as a potential photosensitizer, but it only slowed down the curing and slightly increased the shelf life of the formulation. The increase of Pt concentration to 135 ppm did not accelerate the curing, but reduced the shelf life to 2.5 h. Several experiments were performed at a lower Pt concentration (around 18 ppm); higher dose of UV light was required for curing (7.2 J/cm²), but even at much lower DEADC concentration (around 450 ppm), the shelf life was >30 h. Note that several other compounds happened to be unsuitable as

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2 photosensitive inhibitor: pyrazole (115) (900 ppm) and butylallylmaleate (116) (1800 ppm)
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5 completely prevented the curing even after elevated dose of UV exposure (8 – 10 J/cm²), while
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8 azobenzene (117) (1800 ppm), 1,1'-azobis(cyanocyclohexane) (118 (900 ppm) and 2,2'-azobis(2-
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10 methylbutyronitrile) (119) (900 ppm) were not efficient enough, the shelf life of formulations
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13 containing them being less than 10 min.
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19 DEADC was also studied by Cavezzan *et al* as an inhibitor of hydrosilylation.⁸⁶ Silicone
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21 formulations containing Karstedt's catalyst (60 ppm Pt content) and from 800 to 3000 ppm of
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23 DEADC were subjected to thermal curing (100 °C) with or without preliminary UV treatment
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25 (0.2 sec, Philips type HOK6 UV lamp, linear density 8 kW/m). It was found that at the lowest DEADC
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27 concentration, the curing time could be reduced from 15 to 10 sec by preliminary UV treatment, and
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29 at the maximum concentration, the effect was even more pronounced (from 100 to 15 sec). To explain
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31 the role of the azo compound, the inventors showed by ¹⁹⁵Pt NMR spectroscopy that DEADC forms
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33 a paramagnetic complex with platinum that becomes diamagnetic after UV irradiation, consequently
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35 the platinum is activated and DEADC converted to corresponding hydrazine. More interestingly, in
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37 the range of tested DEADC concentrations (800 – 3000 ppm), the shelf life at 20 °C increased from
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39 6 h to >30 days. The same inventor demonstrated the application of similar hydrosilylation
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41 formulations with DEADC to produce photoresists⁸⁷. The silicone mixture containing 50 ppm of Pt
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43 in form of Karstedt's catalyst and 400 ppm of DEADC was spread on monocrystalline silicon and a
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2 part of the surface was protected with a cover opaque to UV irradiation. Then, the film was exposed
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5 to UV irradiation (Tamarack Scientific Inc. instrument, model PRX 350-4, fitted with a 350W, HBO
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8 type mercury lamp) for 5 min followed by development in toluene for 5 to 10 sec. Adherent
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10 polysiloxane film remained on the irradiated region, while no trace of silicone material could be
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13 detected in the unexposed region.
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17 18 19 *6.3.1. Other photoactive inhibitors.* 20

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22 The GE Company suggested to use dimethylacetylenedicarboxylate (DIMAC, **120**, Figure 25) as
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24 an inhibitor of silicone hydrosilylation that is deactivated by UV light⁸⁸. They did not explain the
25
26 exact role of DIMAC in promoting inhibition. We can suppose that this molecule serves as a ligand
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28 of Pt to generate complexes⁸⁹ not active in hydrosilylation. Whereas, UV-exposure could promote
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30 either isomerization of the complex⁸⁹ or 2+2 photocycloaddition⁹⁰ to release the active Pt catalyst. It
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32 was shown that a formulation of divinyl-PDMS (**1**) with poly(methylhydrogenosiloxane) (**15**)
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34 containing Karstedt's catalyst (25 ppm of Pt content) and 1000 ppm of DIMAC (**120**) could be cured
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36 to smear-free coating by exposure to 1.5 – 4.5 J/cm² (depending on the substrate).⁸⁸ To verify that the
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38 reaction was actually induced by UV light and not by the heat produced by the UV lamp, they tested
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40 the curing under a less powerful lamp (UV Products, Inc. table top lamp, 115 V, 0.35 A. 6 J/(cm²·h))
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42 under temperature control. 2.5 h was required to obtain smear-free surface, while the temperature of
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44 the sample did not change during the exposure (24 °C), confirming photo-activation rather than
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2 thermal curing. To test the shelf life of the studied formulation, the change of viscosity with time was
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5 studied at 25 and at 4 °C. It was shown that in both cases, the viscosity started to increase after 1 h,
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8 and went from 624 to 9000 mPa·s after 24 h of storage at 25 °C. At 4 °C, the viscosity increase was
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11 less noticeable, i.e. from 760 to 1240 mPa·s in 24 h. These results indicate that DIMAC (**120**) does
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14 not completely inhibit hydrosilylation, but only slows down the reaction. Another patent⁹¹ is claimed
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17 to be a continuation of this research, but to our understanding, it does not contain any new
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22 information.
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26 Wacker Chemie AG reported the use of α -diazoketones (**121** – **124**, Figure 25) as photoactive
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28 inhibitors for hydrosilylation catalysts⁹². The mixtures containing divinyl-PDMS (**1**),
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30 poly(dimethylsiloxane-co-methyl-hydrogenosiloxane) (**2**), hydrophobic silica (20%) and Karstedt's
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32 catalyst (30 ppm of Pt content) were used to test the shelf life of photohydrosilylation mixtures in the
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35 presence of these inhibitors (Figure 27). Studied α -diazoketones showed different influence on the
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38 shelf life: the least active diazocamphorquinone (**123**) could extend the shelf life only to 1 day even
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41 at its highest tested content (1000 ppm), while with the most active diazonaphthoquinone (**122**), a
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44 shelf life of more than 3 weeks was achieved. It was also shown that formulations containing 500
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47 ppm of inhibitors **121**, **122** or **124** could be crosslinked by exposure to UV light (365 nm, 250mW)
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50 during 30 minutes after 1 to 15 days of storage. ¹H NMR analyses of a mixture containing Karstedt's
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53 catalyst and 9-diazophenanthrone (**121**) showed that this diazo-compound substituted olefin ligands
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in Pt-complex, this can explain the inhibiting effect of this molecule. Unfortunately, the inventors did not provide any information about the mechanism of photodeactivation of the inhibitor. It can be suggested that exposure to UV-light resulted in photolysis of diazo compound by releasing the N_2 and Wolff rearrangement⁹³⁻⁹⁵ producing substances that are no longer active inhibitors of Pt-catalyst.

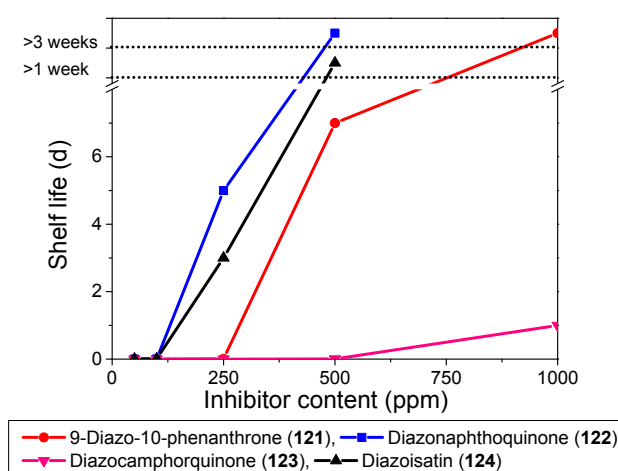


Figure 27. Shelf life dependence of inhibitor content for hydrosilylation formulations containing 30 ppm of Pt in form of Karstedt's catalyst. (Exact values were not reported for “>1 week” and “>3 weeks”)⁹². Lines are only guides for the eyes.

Shin-Etsu Chemical Co., Ltd. reported the use of trialkylphosphites (125 – 127, Figure 25) in combination with Karstedt's catalyst to conduct hydrosilylation under UV light (high pressure mercury lamp, 100 mW/cm², 365 nm)⁹⁶. The inventors prepared mixtures of divinyl-PDMS (1) and poly(dimethylsiloxane-co-methylhydrogenosiloxane) (2) in the presence of 15 ppm of Pt. The longest shelf life (400 h) was achieved with 37 ppm of tributyl phosphite (125) while trioctyl phosphite (126)

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2 (62 ppm) and triphenyl phosphite (**127**) (47 ppm) resulted in slightly shorter shelf life (~350 h). The
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5 formulations with **125** or **127** required 1.5 J/cm² (15 sec) of exposure to get completely cured, the
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8 mixture with **126** was slightly less active and required 2.0 J/cm² (20 sec) of exposure. Later Shin-
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10 Etsu Chemical Co., Ltd. suggested to use radical photoinitiators (**6**, **7**, **11**, Figure 4) in such
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12 formulations to oxidize tributyl phosphite (**125**) and re-activate platinum catalyst^{97,98}. Surprisingly,
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15 the example testing the formulation without any photoinitiator required less exposure (1.5 J/cm²) than
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18 formulations with **6**, **7** or **11** (2.0 J/cm²) to get the same depth of curing (2 mm).
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26 Recently, Bluestar Silicones France SAS patented a photoactivatable inhibiting system for silicone
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28 hydrosilylation curing⁹⁹. They used Karstedt's catalyst (~ 60 ppm of Pt) and 1-ethynyl-1-
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30 cyclohexanol (**105**) as an inhibitor. It was shown that in the presence of 570 ppm of the inhibitor, the
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32 shelf life of the formulation was 25 h, while under the UV light (mercury lamp, 5.6 W/cm²), the resin
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35 cured in 24 minutes. It was also found that the curing could be accelerated by adding a radical
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38 photoinitiator and tris(trimethylsilyl)silane (**128**) (Figure 28). The best result was obtained using
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41 205 ppm of Omnirad 102 (**10**, Figure 4) and 3.6 ppm of tris(trimethylsilyl)silane (**128**), the curing
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43
44 time was reduced to 11 minutes, but shelf life was slightly shorter as well (19 h). The authors claim
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47 that the inhibitor, the photoinitiator and tris(trimethylsilyl)silane (**128**) have synergistic effect
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50 allowing a good inhibition that can be suppressed by UV light, but they did not provide an explanation
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53 about the role of each component of the system.
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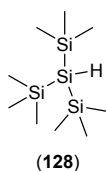


Figure 28. Tris(trimethylsilyl)silane employed by Bluestar Silicones France SAS to accelerate hydrosilylation silicone curing⁹⁹.

7. Photohydrosilylation in 3D printing

One of the very topical application of photo-induced crosslinking is 3D printing¹⁰⁰. The first mentioning of photohydrosilylation for 3D printing is granted to Dow Corning Corporation⁶⁸. They suggested the described-above formulations based on Pt(acac)₂ (**83**) (Section 4.1, Table 2) for 3D printing by several methods requiring photocurable resin (binder jetting, material extrusion, material jetting, stereolithography); here however, examples of actual 3D printing were not provided. Wacker Chemie AG patented 3D printing of silicone elastomer articles by depositing droplets of curable silicone following by UV or IR irradiation (Figure 29a)¹⁰¹. They used formulations containing divinyl-PDMS (**1**), poly(dimethylsiloxane-co-methyl-hydrogenosiloxane) (**2**), hydrophobized silica and (methyl-Cp)trimethylplatinum (**63**) (30 ppm of Pt content). “Bluepoint 4” UV emitter from Dr. Hönle AG, based on high pressure mercury lamp, was used as the UV source. An example of 3D printed object is presented in Figure 29b. It was also demonstrated that vinyl-functionalized MQ-resin can be used to obtain completely transparent 3D printed objects^{101,102}. Later this company suggested the use of poly(ethylene glycol)-based material as a support of silicone resin during printing; such support

could be removed by dissolving in water after the print¹⁰³. This method was further developed by improving the rheology^{104,105} of the formulations and precision of the 3D printing^{106,107}. Finally, the technique was applied to produce anatomical silicone models¹⁰⁸, that were evaluated by surgical residents of the University of California and rated as fairly realistic¹⁰⁹.

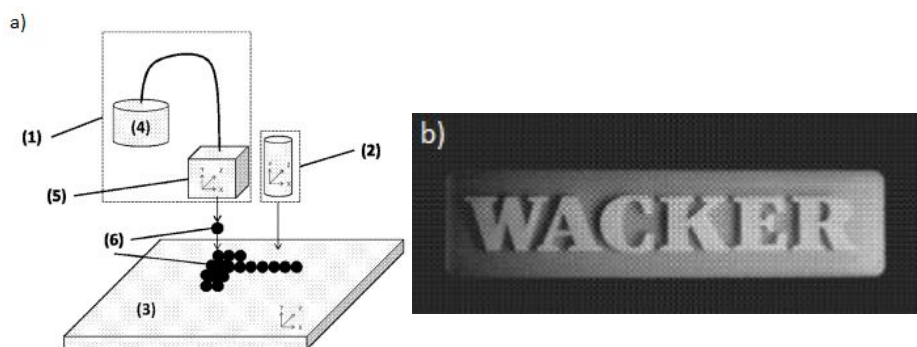


Figure 29. a) Schematic representation of 3D printing: 1) jetting apparatus, 2) source of electromagnetic radiation, 3) base plate, 4) reservoir, 5) printing head, 6) drops. b) An example of 3D printed silicone object (Reproduced from US patent¹⁰¹).

Momentive Performance Materials patented a process for the continuous manufacturing of shaped articles from photohydrosilylation crosslinkable formulations¹¹⁰. They prepared mixtures containing polysiloxane with vinyl groups (14), poly(dimethylsiloxane-co-methyl-hydrogenosiloxane) (2), tetramethyldivinyl-disilazane, OH-terminated PDMS (16), dimethoxy-terminated PDMS (18), (methyl-Cp)trimethylplatinum (63) (4 ppm of Pt content) and from 17 to 29% of fumed silica. These mixtures were shaped by extrusion followed by exposure to the light of iron- or mercury-doped UV lamps. Extruded materials were characterized by hardness from 20 to 51 Shore A and could keep the

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2 shape in time. This work was followed by another one published by Sandler *et al.*¹¹¹. They suggested
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5 to use commercially available UV-curable silicone resin (Silopren UV LSR 2030 by Momentive
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8 Performance Materials) to 3D print drug-loaded drug delivery devices. Although it is not easy to find
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10 information about the composition of the employed commercial resin, there are indications that it
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12 contains (methyl-Cp)trimethylplatinum (**63**)¹¹² and, most probably, a formulation similar to the one
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15 described above¹¹⁰. The formulation was mixed with 0.5 – 1.5% of the drug (Prednisolone) and
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18 applied for 3D printing by extrusion printing with the BioBots 1 Desktop Bioprinter (USA) at room
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21 temperature and under the exposure of LED UVA light source MTE UV303 professional flashlight
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24 (China), with an intensity of 20 mW/cm² and a wavelength of 365 nm. Relatively simple grids were
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27 printed (Figure 30) and property of the material and drug release were studied. Swelling tests were
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30 performed in hexane and it was shown that additional UV post-curing for 3 minutes decreased
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33 swelling degree from 271 to 150 %, as well as reduced soluble fraction from 21 to 5 %. This result
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36 was explained by a higher degree of crosslinking after additional curing and was confirmed by tensile
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39 tests: the sample after additional exposure had 4.89 N load at break, while the sample without post
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42 curing only 3.37 N. The main advantage of the described method of drug carrier manufacture is that
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45 it does not require any heating (all steps are carried out at room temperature), which is important for
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48 heat-sensitive drugs.
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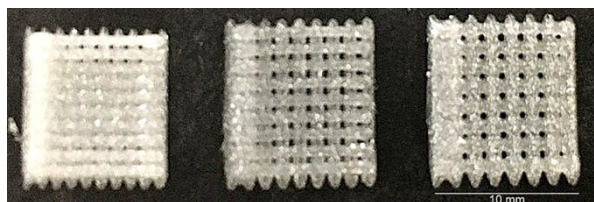


Figure 30. 3D printed silicone drug carriers containing 1% of prednisolone¹¹¹. Reproduced with permission from Elsevier, Copyright, 2018.

8. Conclusive discussion

Starting from the eighties, companies like 3M and GE developed several photoactive catalytic systems for photohydrosilylation. In general, the required time for crosslinking ranges between 10 sec and several minutes, depending on lighting conditions and concentrations applied. From our systematic review, it seems that Cp-based photoactive Pt catalysts allow to achieve a shorter UV curing time than Pt (β -diketonates) or COD-based Pt catalysts^{29,65,69}, but the lack of systematic comparable systems makes this comparison rather difficult. Moreover, it is seen that curing is usually faster under UV light than under visible light^{28,29,34,42,44,60,79} which can be explained by better absorption of UV light by employed catalysts. Photosensitizers and radical photoinitiators are both capable to accelerate the hydrosilylation reaction, but despite the recent interest from academic research groups, there are still no real comprehension about the mechanisms of reaction in the presence of these co-catalysts. Increasing content of catalyst and or co-catalyst was not proved to systematically accelerate curing rates^{44,60,63} except for Cp-based catalyst^{60,65}. On the other hand, large concentrations of

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2 functional groups, both on vinyl and SiH molecules⁶⁸, or more powerful light source³⁴ effectively
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5 reduce the non-smear time. Another striking information from this review is that results can be quite
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8 different between patents and articles, even when they show a priori similar systems^{60,63}. The influence
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11 of dark curing could be a tentative explanation for the observed different reactivities described in
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16 most studies.

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19 If we compare hydrosilylation to other reported light-curing techniques (see Table 3), the first
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22 striking trend is that time for Si-H/Si-Vinyl photo-catalyzed reaction is much longer than usually
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25 required for radical (acrylate or thiol-ene) crosslinking¹⁵. Moreover, hydrosilylation-crosslinking still
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28 occurs in the dark alike cationic photopolymerization. Meanwhile, hydrosilylation formulations are
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31 more attractive as harmless and odorless starting materials. And last but not the least, hydrosilylation-
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34 prepared silicone materials do not contain linkages in the polymer network that could potentially
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37 compromise the final material properties, e.g. in long-term thermal ageing particularly sought for
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42 silicone elastomers.

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46 Photohydrosilylation formulations already found applications as photocurable coatings, materials
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49 for silicone molds, insulators and resins for photolithography. Recently, the examples of 3D printing
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52 using such formulations were demonstrated. Wacker commercialized silicone printing by depositing
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55 droplets of the resin (ACEO company) while Momentive's resin was used for extrusion printing of
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58 drug-loaded objects. This application is probably the most promising for future development of
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2 photohydrosilylation systems. Besides, more active and more controlled catalytic systems could open
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6 up new possibilities for higher resolutions and faster 3D printing. Already described photosensitive
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9 catalysts of silicone hydrosilylation always contain expensive Pt, but there are recent examples in the
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12 open literature of metal-free photohydrosilylation catalysts ^{113,114} that could potentially be exploited
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16 for silicone curing.
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19 Table 3. Basic comparison of different methods of silicone photocuring.
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	Hydrosilylation	Acrylate crosslinking	Thiol-ene crosslinking	Cationic crosslinking
Reaction time	-	+	+	+
Starting material toxicity	+	-	-	-
Price	-	+	+	+
Material properties	+	-	-	-

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54 Author Contributions

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2 The manuscript was written through contributions of all authors. All authors have given approval to
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4
5 the final version of the manuscript.
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10 Funding Sources

11
12
13 This work was supported by a grant from European Union and FEDER Région AURA (project n°
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TOC graph

