ENVIRONMENTALLY FRIENDLY SILICONE PSAs

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1. Introduction

With the growth of world economies, the use of chemicals is increasing in various processes of industrial products. This increased use of chemicals has implications for environmental issues, such as the pollution of the atmosphere, water and ground. In Pressure Sensitive Adhesive (PSA) tapes and release coatings market, Volatile Organic compounds (VOCs) emission to the air is one problem. VOC emissions are one of the causes for photochemical smog, which most countries feel the need to address with regulations. To adapt to this trend, PSA tape market is trying to remove organic solvent from PSA materials. So far, hot-melt, emulsion (Em), and solvent-free UV cure type PSAs are common for eliminating the use of organic solvent, with Em type PSAs being very popular. However, it is difficult to make all PSAs solvent-free without compromising application and performance.

In chapter 1, we will research the situation of world VOC regulations and the ratios of PSA types. Chapter 2 shows the experimental results for high-solid content silicone PSAs and solvent-free silicone PSAs.

1.1 Purpose of VOC regulation and world-wide situation

VOC, nitrogen oxide (NOx) and some chemicals generate photochemical oxidants by UV from sunlight, that leads to photochemical smog. World-wide VOC regulation is in following.

<u>United States</u>

There are several levels of VOC regulations, which are the national, state, and local level. In the national level, the Environmental Protection Agency (EPA) and Clean Air Act Amendment (CAAA) are the most relevant.

The EPA enacted Reasonably Achievable Control Technology (RACT), setting guideline for VOC generation limit and giving guidance for every process to help limit VOC generation. Detail information can be searched from the official EPA website.

Table 1.1 Clean air act guidelines and standards for solvent use and surface coating industry[1].

Industry	Regulation	Regulation/Guideline Type
Paper, Film, and Foil Surface Coating	Paper, Film and Foil Coatings	CTG
Paper, Film, and Foil Surface Coating	Paper and Other Web Coating	NESHAP
Paper, Film, and Foil Surface Coating	Standards of Performance for Pressure Sensitive Tape and Label Surface Coating	NSPS

CTG: Control Technical Guideline
NESHAP: National Emission Standards for Hazardous Air Pollutants
NSPS: New Source Performance Standards

Europe

In 1999, The EU has established the Gothenburg Protocol.

・Germany

From 2001, the Bundes-Immissionsschutzgesetz, Technishe Anleitungzum Reinhal tungder Luft has been applied.

・England

The Environmental Protection Act of 1990 regards VOC as hazardous substance and regulates it. Process Guidance Notes are also adopted as government policy.

Asia

Following the trends in the US and EU, Asian countries are moving toward stricter regulations. China and South Korea are working actively to raise their regulations to the world standard. In Japan, in addition to national regulations, chemical companies are voluntarily working on the development of environmentally friendly processes such as the recovery of organic solvents.

・China

The Ministry of Environment Protection of the People's Republic of China (MEP) has revised Atmospheric Pollution Prevention and Control Law of the People's Republic of China several times. PSA materials require a large amount of chemicals, so Standardization Administration of the People's Republic of China focuses on VOCs regulation by the limitation of VOCs in the production processes of PSA materials at a national level[2].

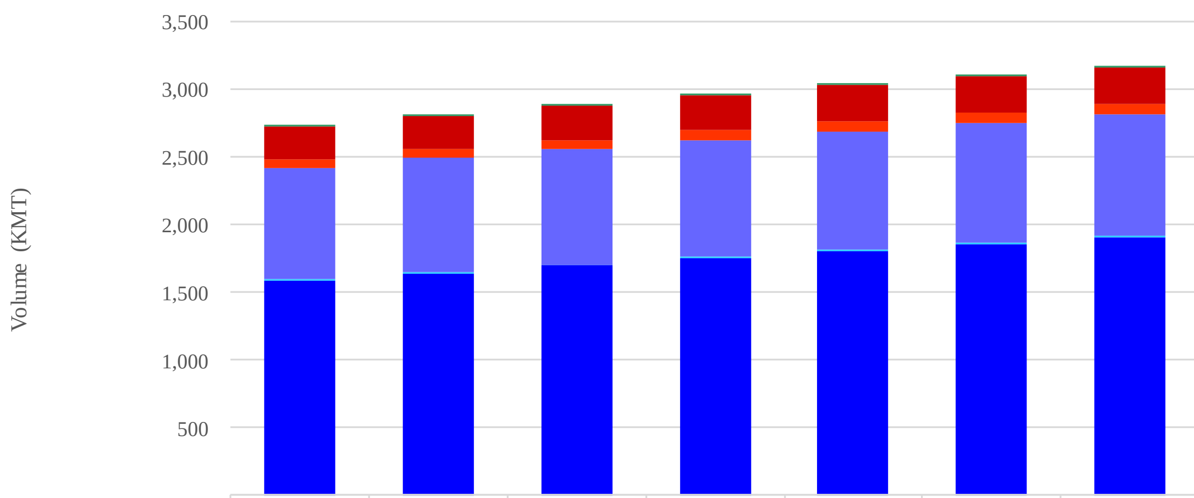
・Japan

The Ministry of the Environment controls VOCs under the Air Pollution Control Law announced in March 2004[3].

1.2 PSA's type, formulation and market

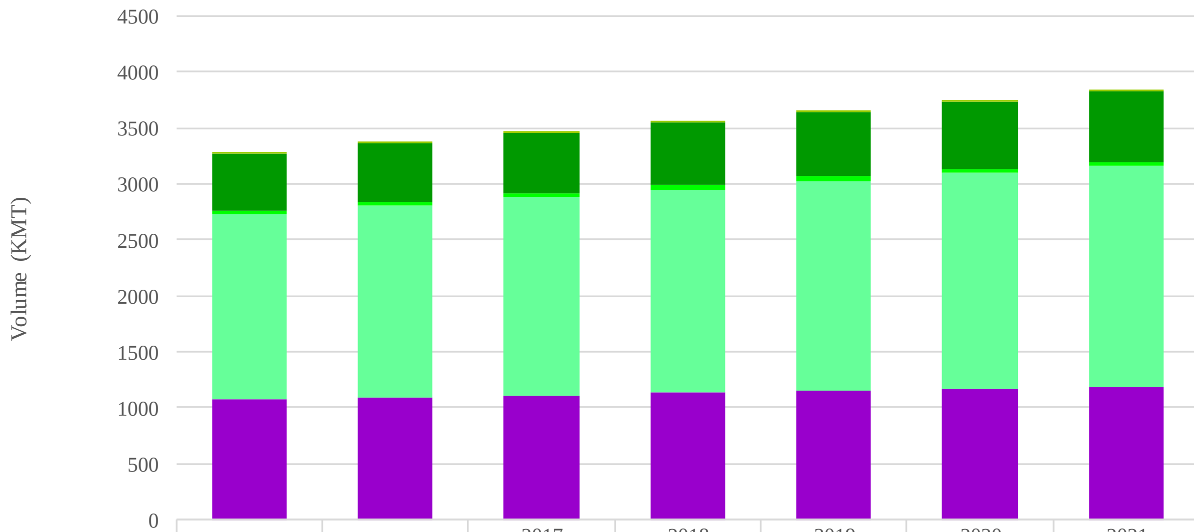
In estimation of 2017[4)], the volumes of acryl, rubber, and silicone PSAs are 2,560KMT, 320KMT, and 8.8KMT respectively. Overall, silicone PSAs are only 0.3% of the total global market.

PSAs are further divided to solvent-based type PSAs, which use organic solvents and solvent-free type PSAs, which do not use organic solvents. Solvent-free type is categorized into Em, hot-melt, and UV cure types. Although the volume of Em and hot-melt type is over half of the market share, solvent-based type PSAs are still used.



	2015	2016	2017 (Forecast)	2018 (Forecast)	2019 (Forecast)	2020 (Forecast)	2021 (Forecast)
Solvent-based silicone	8.4	8.6	8.8	9.05	9.3	9.5	9.7
Solvent-based rubber	240	246	252	258	264	270	276
Latex type rubber	63.8	65.2	66.7	68.2	69.6	71.0	72.4
Solvent-based acryl	826	841	853	864	875	886	896
UV cure acryl	8.2	8.6	9.0	9.4	9.8	10.1	10.4
Em type acryl	1,590	1,641	1,700	1,755	1,810	1,860	1,910

Figure 1.1 Global market volume with PSA types



	2015	2016	2017 (Forecast)	2018 (Forecast)	2019 (Forecast)	2020 (Forecast)	2021 (Forecast)
UV cure	8.2	8.6	9.0	9.4	9.8	10.1	10.4
Hot-melt	511	530	549	568	586	604	622
Calender roll	34.2	35.0	35.7	36.4	37.0	37.6	38.2
Emulsion/Latex	1654	1706	1767	1823	1880	1931	1982
Solvent-based	1074	1096	1114	1131	1148	1166	1182

Figure 1.2 Global market volume with PSA formulations

1.3 Removing organic solvent from acrylic PSA and rubber PSA

Emulsion PSAs seem to be the most environmentally friendly, but in actually there are disadvantages in contrast to solvent-based type and others. For example, the high cost for dry, poor performance in part because of poor waterproofing and chemical change at high temperatures due to the innate properties of emulsifiers. Hot-melt type PSAs also has disadvantages because of their poor heat resistance and additional requirement of a special coating.

A popular topic is solvent-free acrylic PSA. It is an acryl polymer with acryl monomers and acrylic-modified resins with syrup-like consistency that can be cured with UV radiations[5)]. The disadvantage of this type is the remaining acryl monomers after the cure.

Nearly all silicone PSAs are manufactured solvent-based types, and there are peroxide cure type and addition cure type. The reason for this being the difficulty in making solvent-free silicone PSAs due to there being no reactive diluent.

Currently, environmentally friendly products consist of high solid content or non-aromatic solvent type. This lead into the goals of silicone PSA R&D which are to make “environmentally friendly” and “better performance” PSAs. Silicone PSAs can stick various surfaces making the area of applications wider if solvent-free type PSAs can be achieved from a technical standpoint.

2. Environmentally friendly silicone PSA

Silicone PSAs made from PDMS shows high heat resistance, good low temperature performance, weatherproofing, good electrical insulation and good chemical properties. These PSAs are coated on various backings and made for PSA products like tape. It consists of high molecular weight (Mw) PDMS and MQ resin, which is provided solvent-based type using toluene or xylene.

For environmentally friendly materials, PSAs with a high solid content, without aromatic solvent, or solvent-free are the most relevant for VOC limitation. The following data shows the relationship between Mw of the base polymer and PSA properties and the effect of using non-aromatic solvents for silicone PSAs.

2.1 Silicone PSA

Silicone PSAs are used for various applications like in below:

- For high heat resistance applications : heat resistant tapes, masking tapes for electrical device/plasma/solder
- For adhesion to various surface : splicing tapes for silicone release liner, tapes for silicone rubber / fluoro resin / polyolefin
- In electrical insulation : binder for mica tapes, electrical insulation tapes
- Low reactivity to living organisms : skin contact application
- Removability and transparent : protective film for optical applications

<u>Formulation of silicone PSA</u>

Silicone PSA consists mainly of high molecular PDMS (Gum) and silicone resin (MQ resin) with some organic solvent. Table 2.1 shows each components of PSAs. Gum is the base polymer of silicone PSAs and MQ resin is the tackifier.

Table 2.1 Several PSAs and their components

	Silicone PSA	Acrylic PSA	Rubber PSA
Base	High Mw PDMS (Gum)	Polyacrylate	Natural rubber Synthetic rubber
Tackifier	Silicone resin (MQ resin)	(Rosin, terpene resin, petroleum resin, e.g.)	Rosin, terpene resin, petroleum resin, e.g.

<u>Structure of Gum and MQ resin</u>

Gum is straight-chain polymer consist of the D units shown in figure 2.1. The functionality groups (R groups) depicts the organic groups. Although methyl groups are the main functional group, other groups such as phenyl or vinyl are also used in PSAs to for effect its properties. Gum has about hundreds of thousands Mw and seems to be solid, but it flows and change its shape as time goes by so it is a kind of high viscosity liquid. Gum shows good removability from adherends.

MQ resin is small polymer composed of M and Q units as shown in figure 2.1. The Mw of MQ resin are in the thousands and is a fragile solid in room temperature (RT). Usually it is used with solvent for better handling.

Figure 2.2 features an example of gum and MQ resin. Blending of the MQ resin and the gum doesn't generate enough performance. Condensation of Si-OH of gum and Si-OH of MQ resin improved cohesion of PSA. But, MQ resin is rich in silicone PSAs formulation, so most of MQ resin doesn't have chemical bond with gum.

R	R	$O_{1/2}$
R-Si-$O_{1/2}$	$O_{1/2}$-Si-$O_{1/2}$	$O_{1/2}$-Si-$O_{1/2}$
R	R	$O_{1/2}$
M unit	D unit	Q unit

Figure 2.1 Units of polysiloxane

Figure 2.2 Picture of gum and MQ resin

Peroxide cure type and addition cure type

The adhesion of silicone PSAs cannot achieve a significant level with the removal of organic solvent from the formulation alone. As a result, cross-linking of the material is required. There are several different curing/cross-linking mechanisms available. Table 2.2 shows each characteristic.

Peroxide cure type PSAs make cross-linking by benzoyl peroxide (BPO) or other peroxides. BPO generates methyl radicals from methyl group of gum eventually leading to the radicals reacting each other. 150°C or more is required for curing and making it necessity for the backing of the tape to be able to endure high temperatures. Benzoic acid (by-product of BPO) remains in the PSA layer with insufficient cure conditions. On the other hand, the advantages of peroxide cure types are the lack of inhibitors for the catalyst and a long pot life.

In addition cure type PSAs, cross-linking occurs by a reaction of a vinyl group and a Si-H group catalyzed with a platinum group compound. This reaction requires a lower temperature than peroxide cure types, which allows for backings with lower heat resistances. Some of the disadvantage of addition cure types are inhibitors for the platinum group catalyst. This catalyst is easily inhibited by N, P, S, Sn-containing compounds. We have to avoid contamination with these chemicals. An examples of inhibitors is the tin catalyst for condensation cure type silicones.

Table 2.2 Characteristics of each cure type

	Peroxide cure type	Addition cure type
Reaction	$2Si\text{-}CH_3 \rightarrow 2Si\text{-}CH_2\cdot$ $\rightarrow Si\text{-}CH_2\text{-}CH_2\text{-}Si$	$Si\text{-}CH{=}CH_2 + H\text{-}Si$ $\rightarrow Si\text{-}CH_2\text{-}CH_2\text{-}Si$
Characteristic	High temperature cure (150~180°C, over 2min), Heat resistant backing only (Polyimide, glass fiber, etc.)	Low temperature cure (90~130°C, over 30 sec), Poor heat resistant backing is acceptable (PET, etc.)
	No inhibitor for reaction	Inhibition for reaction
Adhesion	400~800gf/inch	10~800gf/inch

2.2 High solid content silicone PSA

Silicone PSAs are usually provided as solvent-based formulations because of its ease of handling during production. Several methods will be explained for reducing organic solvent.

Silicone PSAs contains approximately 40~50 wt% of toluene or xylene. Lowering the organic solvent to silicone ratio in the formulation enables reduction of organic solvent in exchange for a higher viscosity. This is because increasing MQ resin ratio in formulation. Lowering the viscosity of the gum itself will help with lowering the viscosity of the overall mixture.

Peroxide cure type PSAs benefits from higher Mw gum for shear adhesion. Additionally, cross-linking is required for better performance. Increasing the amount of BPO could be a solution, but the maximum cross-linking density has a limiting threshold even if BPO is overused. Lower Mw gum helps decrease the viscosity of formulation, but share adhesion is worsened.

In addition cure type PSAs, cross-linking density can be controlled by changing the amount of vinyl groups in the gum. This results in the ability for addition cure type PSAs to have a high cross-linking density while achieving a low Mw gum with good shear adhesion.

Table 2.3 and 2.4 show results of the adhesion, loop tack and shear adhesion failure temperature (SAFT) for several PSAs with a range of 200,000~400,000 Mw. Using higher Mw gum gives a higher viscosity for the silicone PSA formulation.

Table 2.3 shows that the adhesion and loop tack of peroxide cure type have no relationship with the Mw of gum, but SAFT is higher with higher Mw gum.

From table 2.4, the Mw does not impact the adhesion and loop tack of several addition cure type PSAs don't matter with Mw of gum same as peroxide cure type PSAs. And, SAFT also has same trend. This is different from peroxide cure type. All addition cure type PSAs show a SAFT of 300°C in the evaluation. As a result, the slip distance was tested and no difference was found.

As the data shows addition cure type PSAs are more suitable for high solid formulations because of the high SAFT when compared to peroxide cure type PSAs despite having a lower Mw, and by default, lower viscosity.

Table 2.3 PSA properties of peroxide cure type (75% silicone content)

Mw of gum	Viscosity of PSA (Pa·s)	Adhesion (gf/inch)	Loop tack (gf)	SAFT (°C)	Slip distance* (mm)
230.000	73	790	1,940	228	0.62
270,000	128	790	2,000	246	0.39
320,000	215	810	1,900	257	0.25
360,000	335	790	2,020	257	0.21
380,000	481	850	1,720	262	0.20

Formulation: Silicone / BPO = 100 / 2
Backing: 25µm polyimide
PSA thickness: 40µm
Adherend: SUS304 (polished with #280 for reuse)
*Inch x inch tape slip distance after 200°C/1h aging for shear adhesion evaluation.

Table 2.4 PSA properties of addition cure type (75% silicone content)

Mw of gum	Viscosity of PSA (Pa·s)	Adhesion (gf/inch)	Loop tack (gf)	SAFT (°C)	Slip distance *(mm)
210,000	28	870	2,130	>300	0.19
270,000	51	730	2,080	>300	0.21
300,000	87	760	2,110	>300	0.13
350,000	173	720	1,970	>300	0.14
400,000	238	810	2,010	>300	0.17

Formulation: 40ppm Pt for silicone
Backing: 25μm polyimide
PSA thickness: 40μm
Adherend: SUS304 (polished with #280 for reuse)
*Inch x inch tape slip distance after SAFT test for shear adhesion evaluation.

2.3 Silicone PSA without aromatic solvent

Conventional silicone PSAs are made with aromatic solvents such as toluene and xylene because MQ resin is manufactured in these solvents. Toluene has acute toxicity as well as irritation to the mucous membranes when exposed to toluene. Xylene, like toluene, is toxic but is also carcinogenic with 2-ethylbenzene.

We tried to use isoparaffin, which is free of toluene and xylene, for the production of silicone PSAs. Isoparaffin has the benefit of being non-irritative, as it is a compound found in cosmetic applications. It has the added benefit of having good performance for wetting the backing via lowering of the surface tension.

In peroxide cure type PSAs, polar solvents like methyl isobutyl ketone, ethyl acetate, or propylene glycol monomethyl ether acetate should be used with isoparaffin because isoparaffin cannot dissolve BPO.

Addition cure type, Mw of gum can be decreased, so the viscosity of PSA can be lower. Conventional silicone PSA should be 40% content or lower for coating, however, PSA using lower Mw gum can be coated with 70% content.

Little solvent remains in PSA after cure, so toluene and xylene would stay little in cured PSA layer for conventional silicone PSA. In order to avoid the issue, we have to make MQ resin in organic solvent without toluene or xylene. It is possible to make MQ resin in isoparaffin technically.

Table 2.5 and 2.6 shows the adhesion of silicone PSAs with toluene or isoparaffin. 0 day means adhesion of just after coating, and others are adhesion for several days aging with laminating fluorosilicone liner for covering sticky surface. All PSAs have a trend for a little decreasing adhesion with time, but adhesion of 0 day and 14 days are same, so similar PSA properties can be obtained in either solvent.

Table 2.5 Adhesion of peroxide cure type PSA with aging

Silicone content (%)		76		75	
Viscosity (Pa·s)		115		101	
Solvent in PSA		Toluene		Isoparaffin C*	
Solvent for dilution		Toluene		Ethyl acetate / Isoparaffin E*	
Aging condition		23°C/50%RH	60°C/90%RH	23°C/50%RH	60°C/90%RH
Adhesion (g/inch)	0 day	940	940	870	860
	1 day	880	900	770	760
	7 days	850	810	730	730
	14 days	790	790	740	740

Formulation: Silicone / BPO = 100 / 2
Backing: 25μm polyimide
PSA thickness: 40μm
Adherend: SUS304 (polished with #280 for reuse)
*Isoparaffin solvent from Exxon Mobil

Table 2.6 Adhesion of addition cure type PSA with aging

Silicone content %)		88			
Viscosity (Pa·s)		23			
Solvent in PSA		Isoparaffin C*			
Solvent for dilution		Toluene		Isoparaffin E*	
Aging condition		23°C/50%RH	60°C/90%RH	23°C/50%RH	60°C/90%RH
Adhesion (g/inch)	0 day	850	850	840	860
	1 day	800	800	820	820
	7 days	800	820	820	850
	14 days	790	800	810	770

Formulation: 40ppm Pt for silicone
Backing: 25μm polyimide
PSA thickness: 40μm
Adherend: SUS304 (polished with #280 for reuse)
*Isoparaffin solvent from Exxon Mobil

2.4 Solvent-free silicone PSA

There is a market demand for reducing solvents found in cured layer of PSAs in application like electrical insulation tapes, heat resistant tapes, masking tapes and carrier tapes for electrical devices when in use for closed working space like cleanroom.

Removing all solvent from silicone PSA formulations lowers fluidity at RT. The 210,000 Mw gum measured has a lower than usual Mw gum that is for general PSAs. An example of this is shown in Figure 2.3, where the relationship between temperature and viscosity is shown for these solvent-free formulations of the same gum/MQ resin ratio. Even at high temperature of 150°C, the fluidity of high Mw gum is still low, so the viscosity cannot be measured. Gum with a Mw of 85,000 and 60,000 was also tested. It is a liquid at RT, but in a formulation, these gums cannot have its viscosity measured due to a lack of fluidity like the 210,000mw gum. It is possible to measure the viscosity of formulation at 120°C or above, but we cannot measure the viscosity of the formulation in RT.

As mentioned, PSA properties do not change with different Mws if cross-linking density is kept constant, however, using lower Mw base polymer that is functionalized with vinyl groups leads to a higher cross-linking density, which results in a PSA that is less soft and therefore has less adhesion.

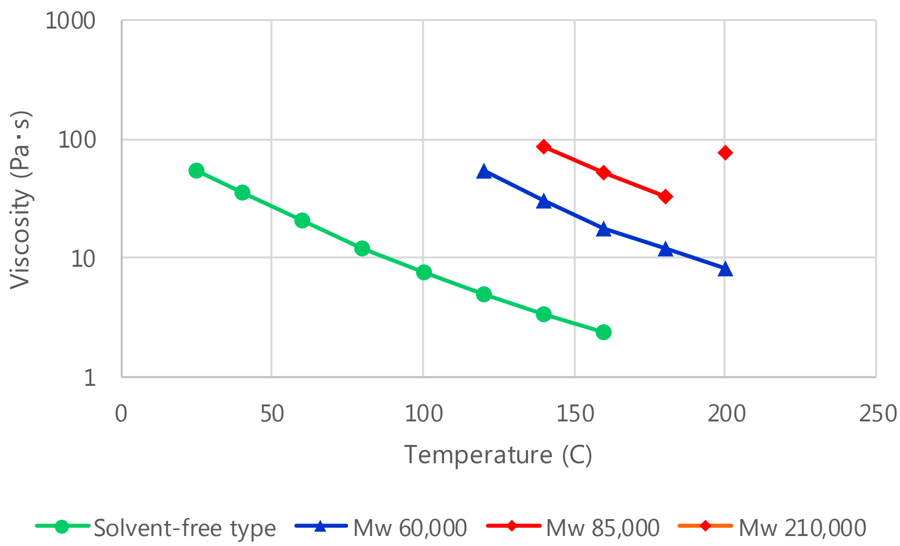


Figure 2.3 Temperature-viscosity relationships for solvent-free formulations.

Low adhesion silicone PSAs can be obtained in solvent-free formulations by controlling the base polymer's Mw and ratio of gum/MQ resin. PSA properties of low adhesion type and super low adhesion type are in Table 2.7. These types of PSAs can be coated without organic solvents. In addition, it is possible to coat a thicker layer and can form more than a 10 mm thickness of cured material. It can be applied as a gap filler between glass and flat panel displays.

Compared with conventional silicone PSAs, these types of PSAs have lower viscosity. For tape applications, toluene-free primer for silicone PSAs is also available.

Table 2.7 Properties for solvent-free-silicone PSAs

PSA	Low adhesion type	Super low adhesion type
Silicone content (%)	100	100
Viscosity (Pa･s)	55	50
Adhesion (gf/inch)	110	10
Total light transmission (%) (Blank: 90.4)	91	92
Haze (%) (Blank: 1.0)	0.7	0.8
Hardness (Asker C)	10	30
Refractive index	1.41	1.41

3. Conclusion

VOC control is world-wide challenge and that affects all markets. The PSA tape market adapts to this challenge by conducting formulation studies for a solvent-free PSAs.

From our research, addition cure type silicone PSAs have an advantage for reducing solvent in their formulation. Isoparaffin can be used for silicone PSA as solvent without affecting properties that are desired from conventional PSAs made with toluene. Although making high adhesion type PSAs is difficult using solvent-free formulations with the current technology, it is still possible to make low adhesion type PSAs with low Mw base polymer.

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