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Development of the low-odor and non-flammable SGA and its applications

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Abstract

Nowadays, especially concern about the odor produced in the operations of adhesion is increasing by enhancement of environmental awareness.

The second generation acrylic adhesive (SGA) is used abundantly as an assembly method replaced with welding or a bolt and nats at the assembly of the metal construction.

However, an odor may become a trouble of adhesion although adhesion performance is good.

Although the main raw material of many SGA(s) is a MMA monomer, the odor of MMA is very strong and it is a key factor of an adhesive odor.

While lowering the odor of an adhesive by excluding a MMA monomer from formation of an adhesive, it is indispensable to improvement in property of an adhesive.

We considered special monomers selection installation from many low odor acrylic monomers, and developed the low-odor SGA with high adhesion property which does not contain a MMA monomer.

These low-odor SGA are non-flammable liquids and not classified as “CLASS 3-FLAMMABLE LIQUIDS (UN Recommendations on the Transport of Dangerous Goods)” .

Furthermore, it is characterized by the tolerance level of the wide mixing ratio and a capability of oily surface adhesion.

They also have a unique feature that curing conditions can be identified by “Color Change” of adhesives.

Adhesives are applied for an assembly of metal housings, and production of honeycomb sandwich panels.

We make it the fundamental concept to supply a new assembly method to a customer by the low-odor SGA.

This report describes the property and its application case of the low odor SGA in detail.

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Low-odorization concept and characteristics of SGA

Table.1 The conventional composition and MMA removal composition

Conventional		MMA removal	
Monomers	Vapor pressure hPa	Monomers	Vapor pressure hPa
MMA $CH_2=C(CH_3)C(=O)O-CH_3$	20 Same as toluene	2-HEMA $CH_2=C(CH_3)C(=O)O-CH_2OH$	1.2
2-HEMA $CH_2=C(CH_3)C(=O)O-CH_2OH$	1.2		

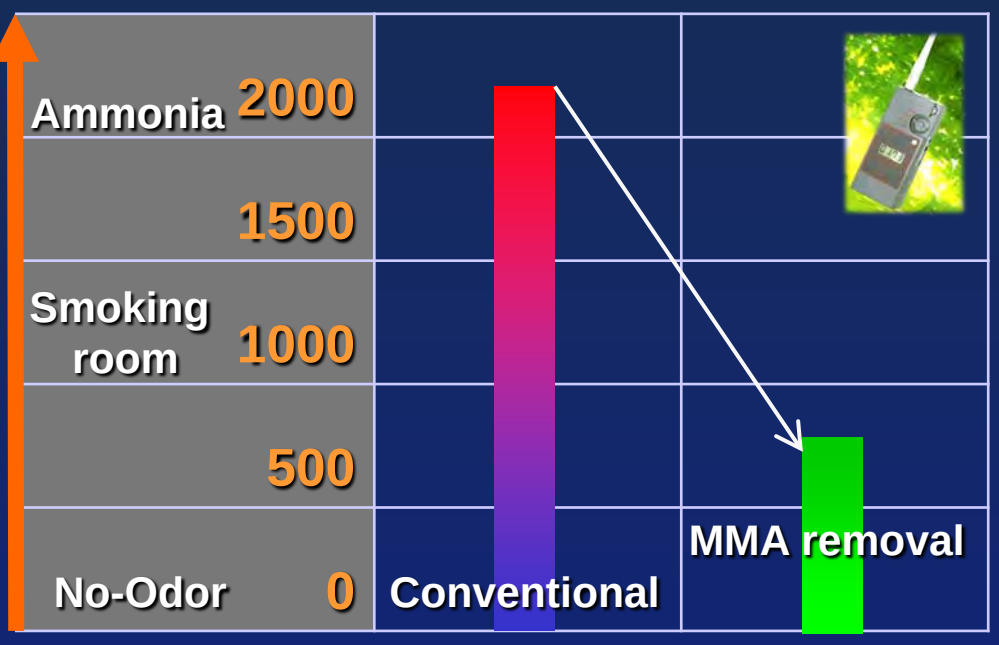


Fig.1 Comparison with an odor sensor

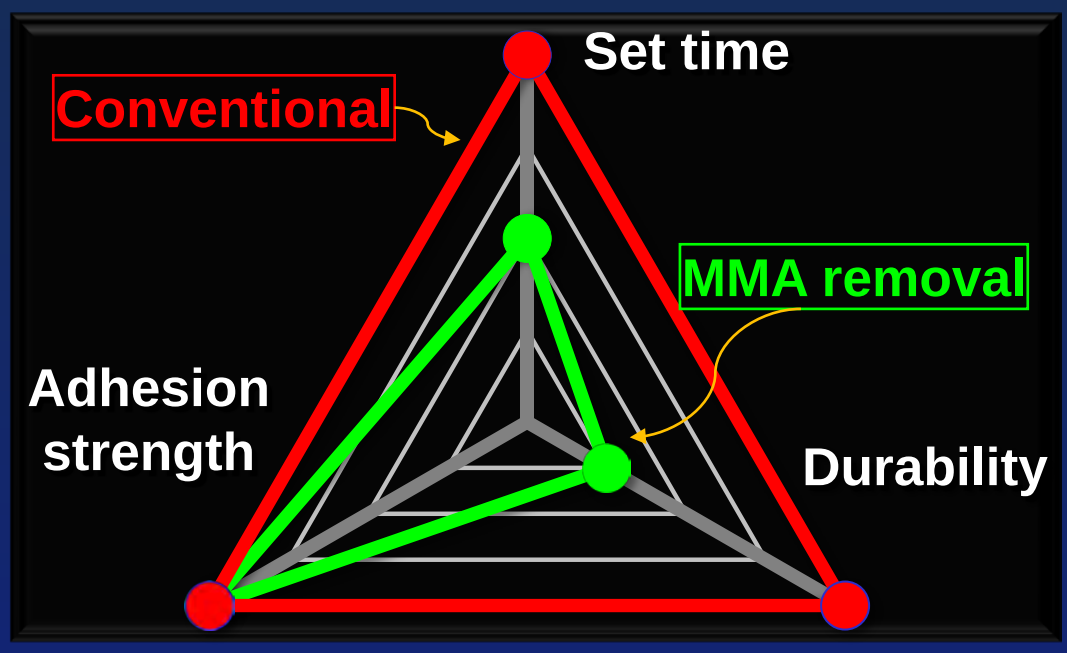


Fig.2 Characteristics comparison

■ Although the odor of the monomer of a low vapor pressure is low, there is a defect which cannot take balance of characteristics.

Table.2 An acrylics monomer and a vapor pressure

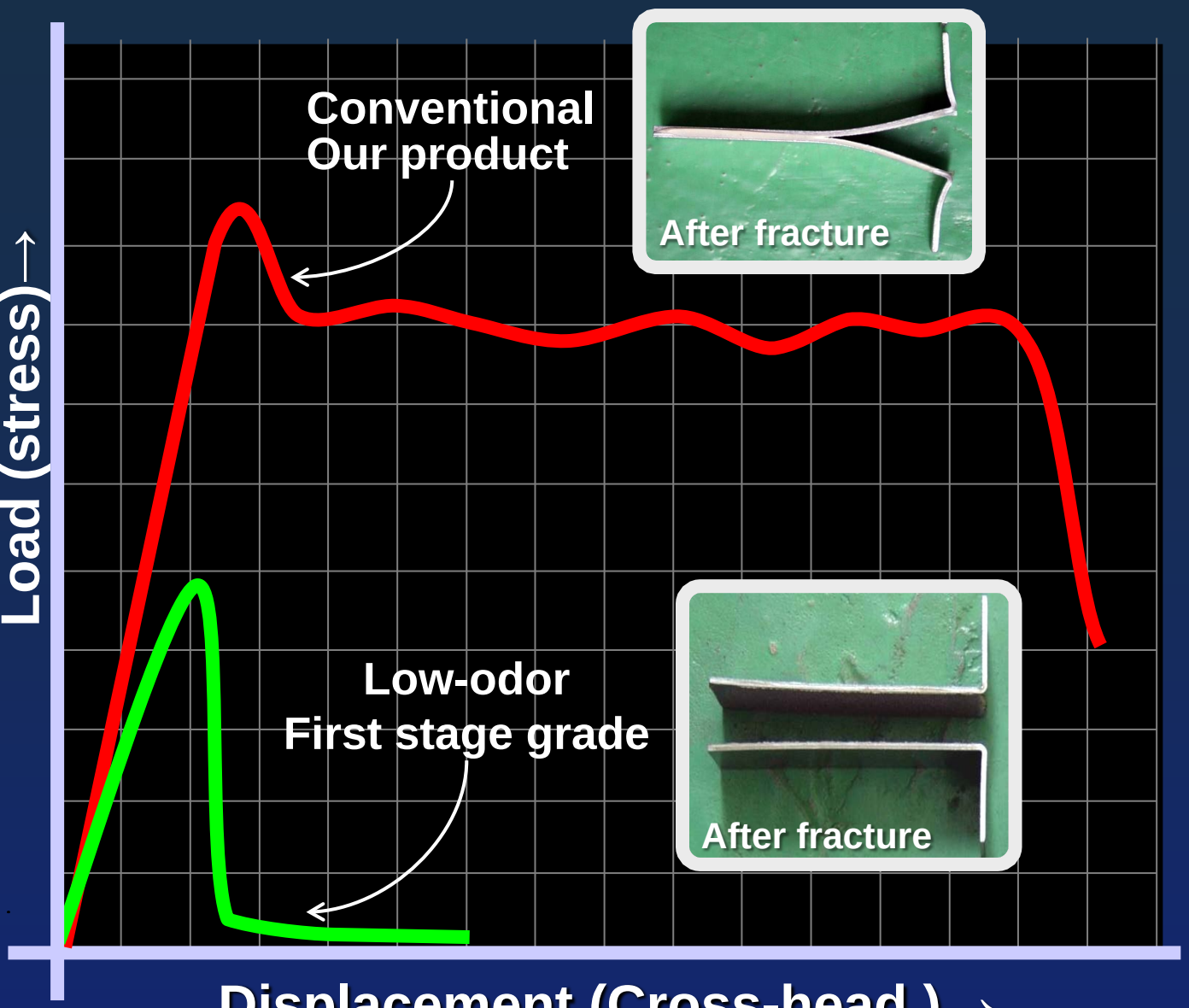
Monomers	Vapor pressure	Characteristics
2-Hydroxypropyl methacrylate $CH_2=C(CH_3)C(=O)O-CH_2CH(OH)CH_3$	1.2 hPa	High strength
Phenoxyethyl methacrylate $CH_2=C(CH_3)C(=O)O-CH_2CH_2O-C_6H_5$	2.3 hPa	High durability
Acrylic oligomer $CH_2=C(CH_3)C(=O)O-(CH_2CH_2)_n-C_6H_4-C(CH_3)_2-C_6H_4-(CH_2CH_2)_n-OC(=O)C(CH_3)=CH_2$	1.4 hPa	Curering speed

Selection

■ Low-odorization concept

Introduce these monomers and offer new technology by developing low-odor adhesives with the good characteristics of balance.

Improvement approach of toughness



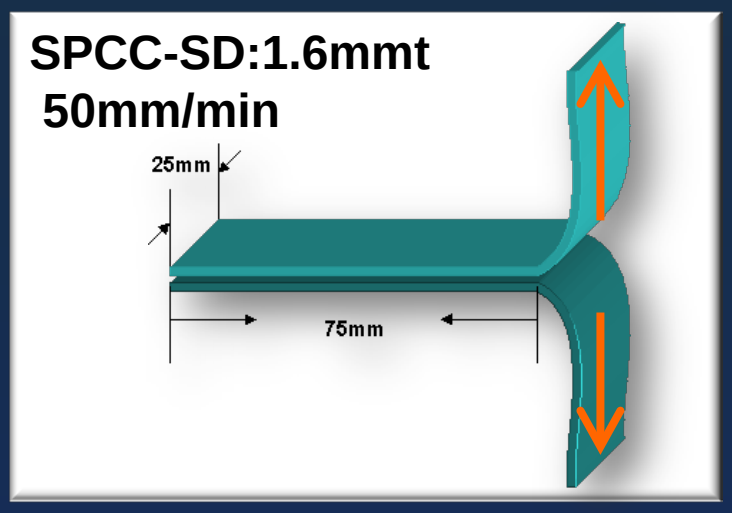


Fig. T-peel Test piece

Fig.3 Typical chart-pattern of low-odor first stage grade in T-peel test.

- The conventional grade is high load and its deformation of a test piece is large.
- Low-odor first stage grade is low strength and no deformation of a test piece.

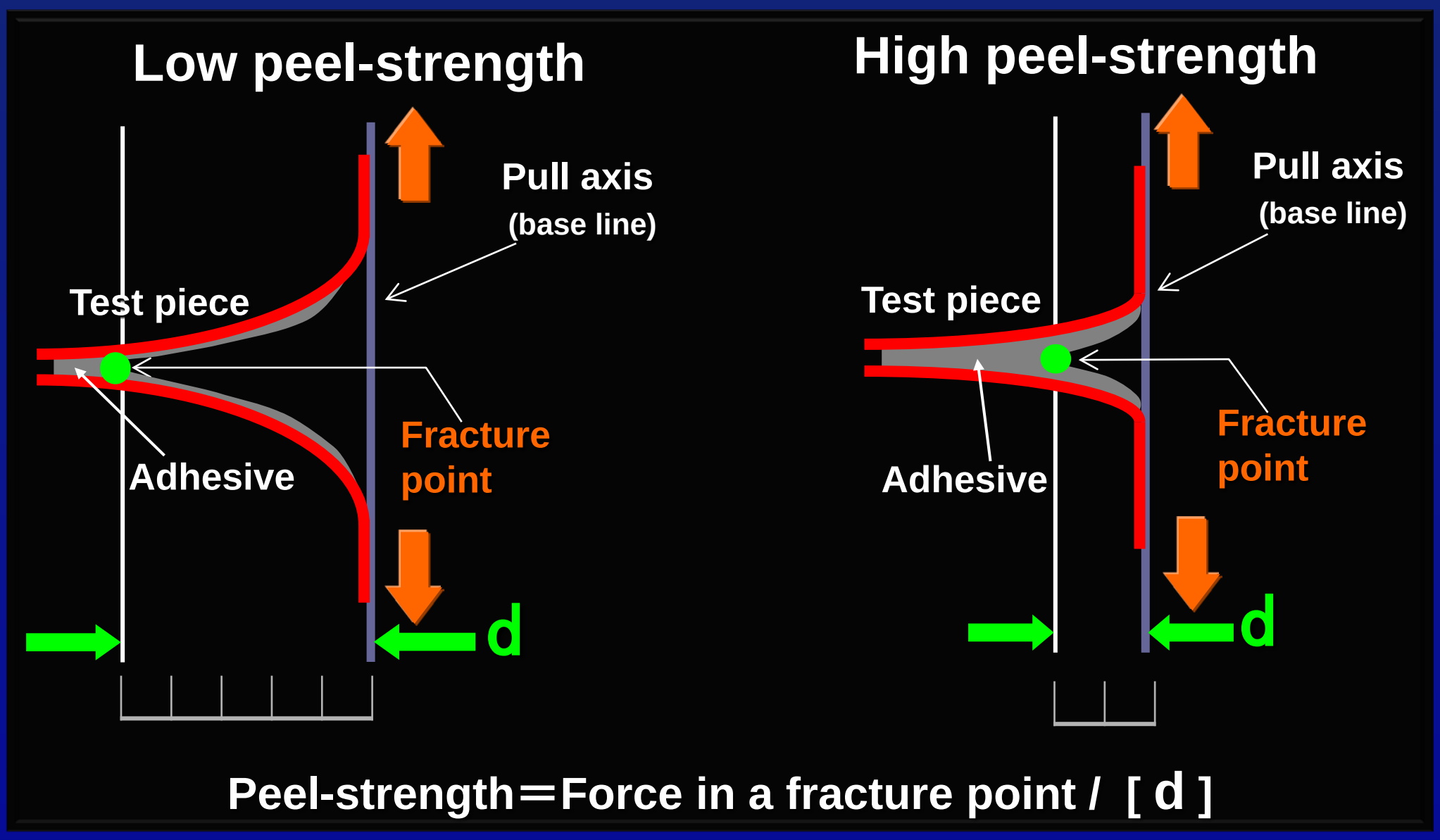


Fig. 4 Test- piece mimetic diagram in a peeling test

- If toughness is given to adhesives, the length of a fracture point will be controlled and high peel strength will be obtained.

Approach by an elastomer hybrid of NBR and MBS

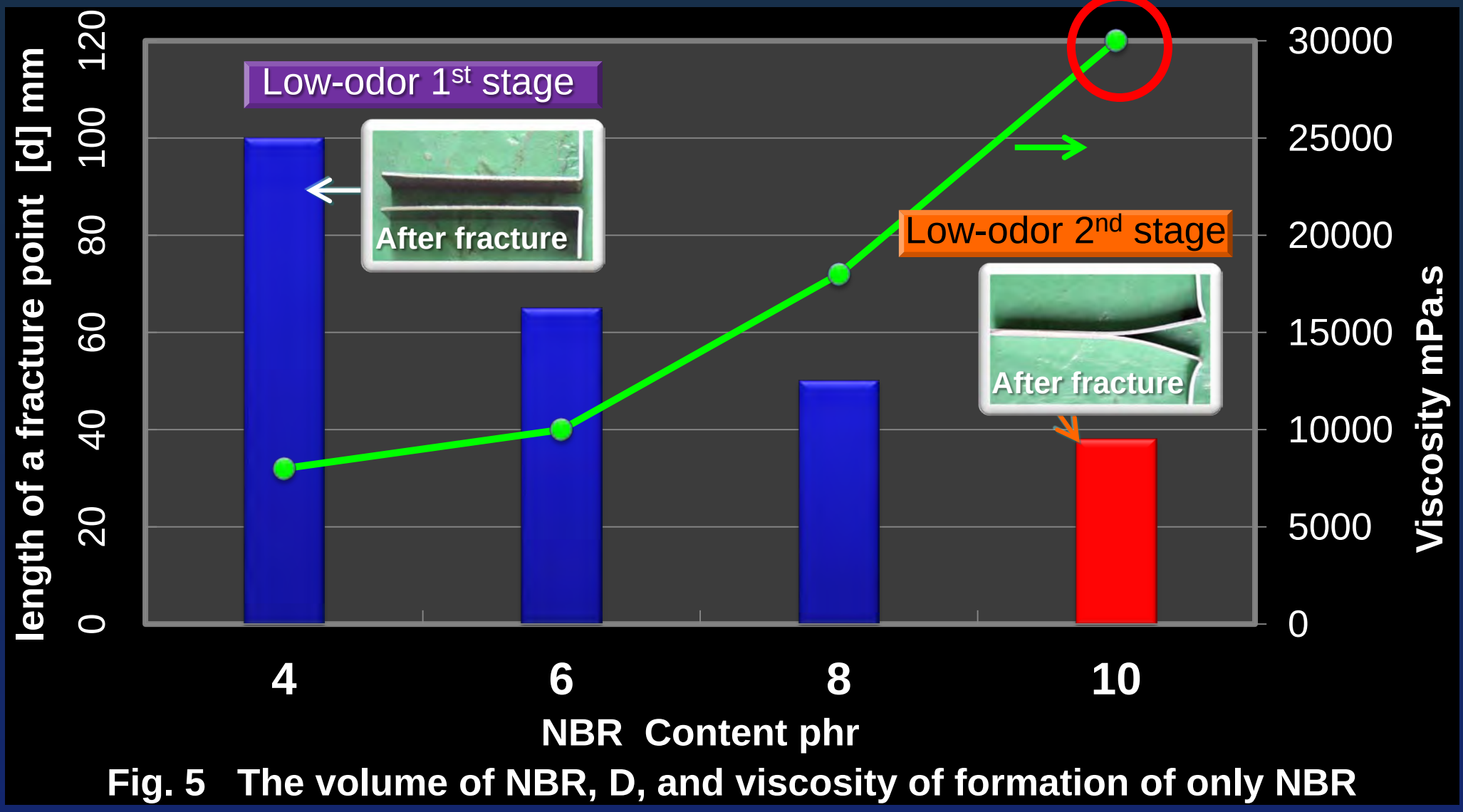


Fig. 5 The volume of NBR, D, and viscosity of formation of only NBR

■ With the increase in NBR concentration, the fracture point [d] was short compared with the 1st-stage grade, and toughness was given. But because the viscosity of adhesives was high, it was expected that an application is difficult.

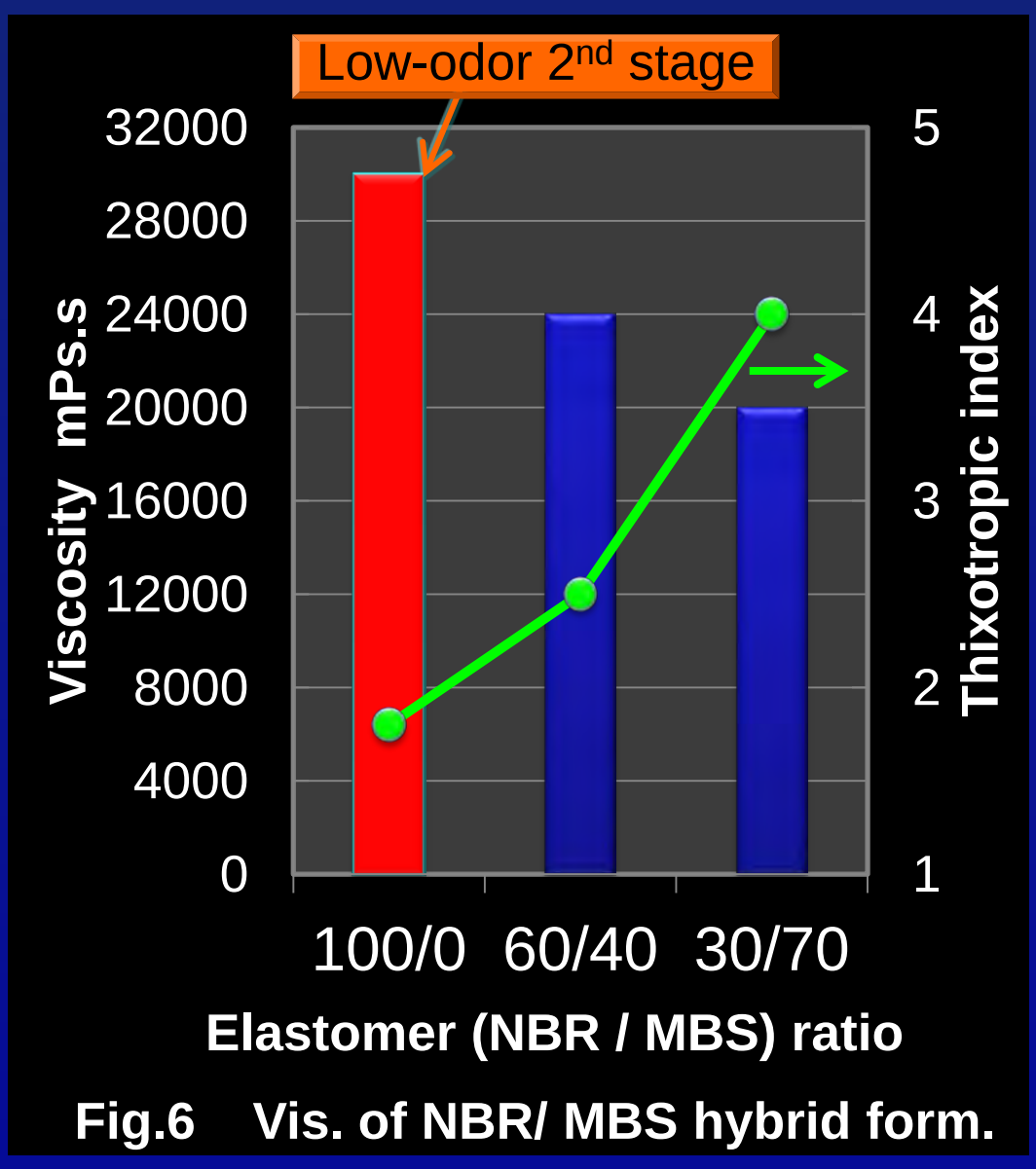


Fig.6 Vis. of NBR/ MBS hybrid form.

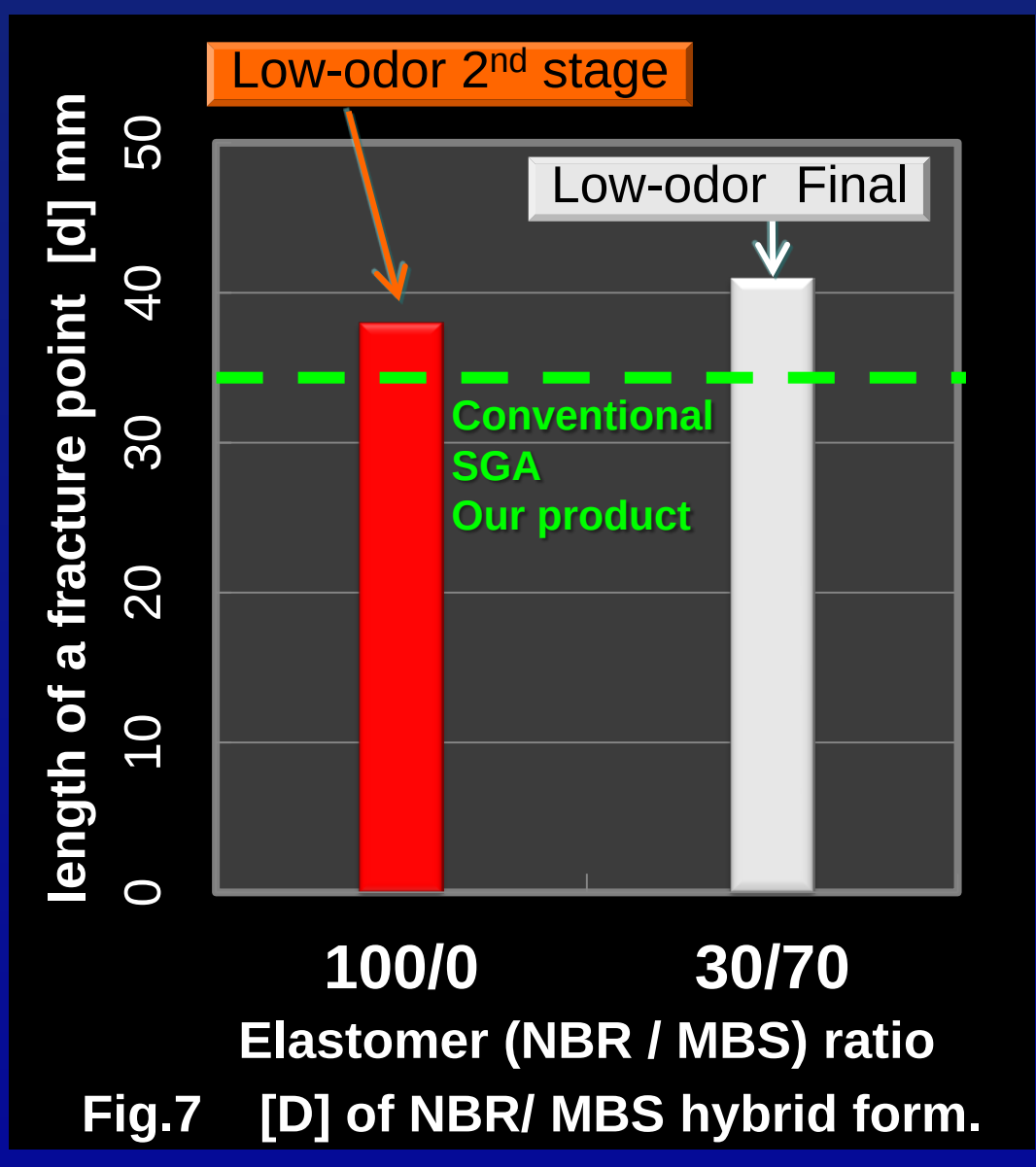


Fig.7 [D] of NBR/ MBS hybrid form.

■ Hybridization of NBR and MBS attained improvement in the reduction in viscosity, and thixotropy as an elastomer component. And fracture point [d]and toughness of a hybrid formula are the similar level as the conventional grade.

Characteristics of a low-odor development grade

Table.3　Sag-test of a low-odor development grade

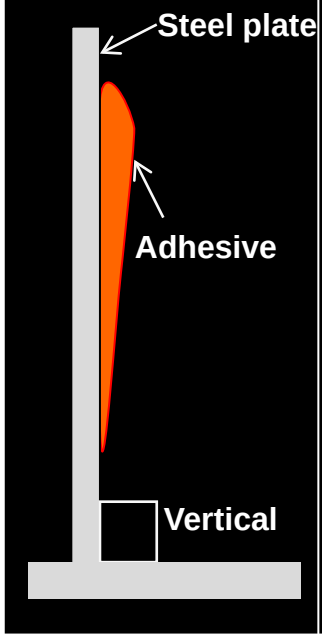
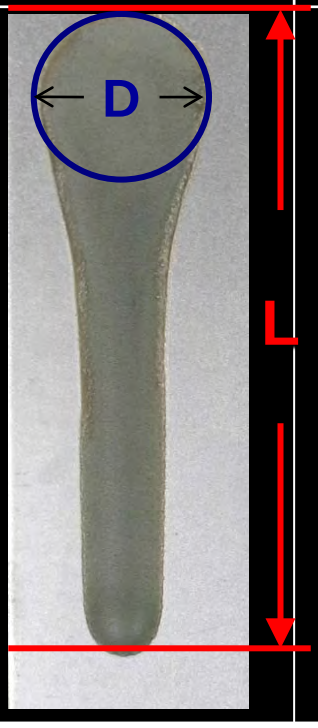
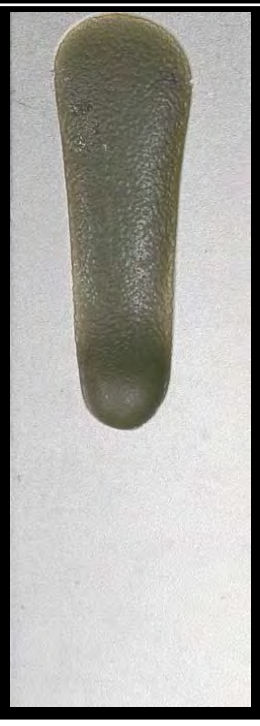
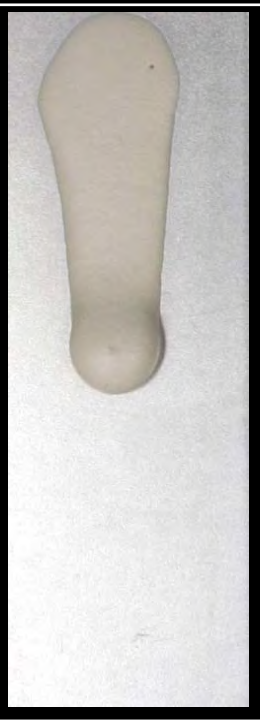
item	Vertical Sag - test		
	Low-odor 1st stage	Low-odor development	Conventional SGA
Diameter D mm	16	13	13
Sag length L mm	64	41	38
Method				

Fig.8　Actual sag (1st stage grade)

■ Thixotropy is high because of a NBR/MBS hybrid design, sag is extremely improved compared with a first-stage grade, and a low-odor development grade (the final grade) is the similar sag level as the conventional grade.

Table. 4　Typical formation of low-odor and non-flammable NS700 series

Low-odor and non-flammable SGA NS700 series Flash point :101℃		Conventional SGA Our product Flash point :21℃>	
NBR	1-5%	NBR	10-20%
MBS	10-15%	-	-
Phenoxyethyl methacrylate Flash point :120℃	30-40%	Methyl methacrylate Flash point :11℃	40-50%
2-Hydroxypropyl methacrylate Flash point :104℃	20-30%	2-Hydroxyethyl methacrylate Flash point :114℃	10-20%
Acrylic oligomer Flash point :230℃	5-15%	-	-
Initiator :**Cumene hydroperoxide**		Initiator :**Cumene hydroperoxide**	
Accelerator :**Vanadylacetylacetonate**		Accelerator :2-Imidazolidinethione	

■ Monomer formation was considered as the 3 types monomer design which does not completely use MMA from the odor (vapor pressure) with property balance.
■Adhesives form only monomers of a high flash point and the flash point of adhesives is conventionally higher than a grade.

Characteristics of low-odor and non-flammable SGA

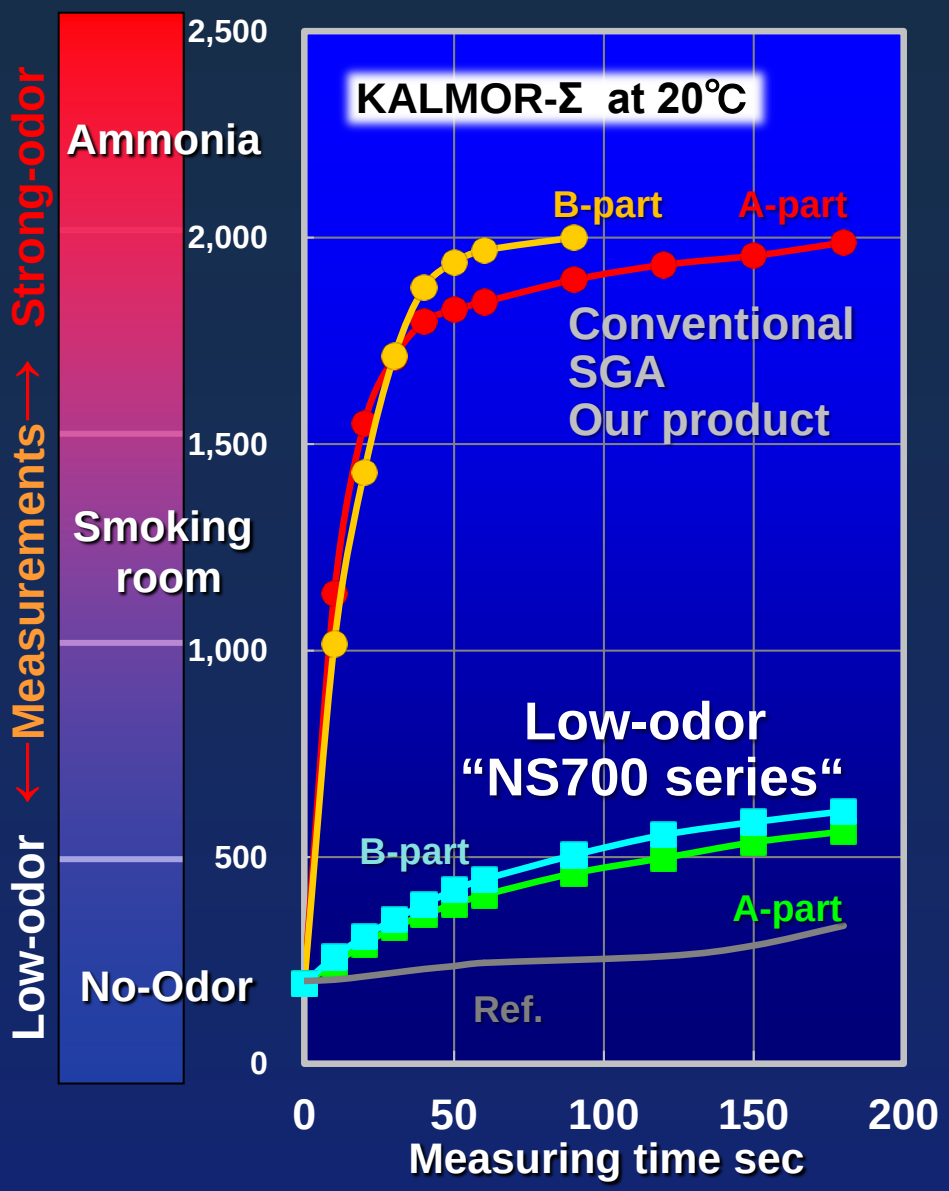


Fig.9 Odor of low-odor and non-flammable SGA

Table. 5 UN Recommendations on the Transport of dangerous goods

Conventional SGA 20℃	Flash point	Low-odor NS700 series 101℃
FLAMMABLE LIQUIDS CLASS 3	61℃	Non-FLAMMABLE LIQUIDS

- Odor of development grade NS700 series is hardly sensed compared with the conventional grade.
- Flash point of the development grade NS700 series that MMA is not contained is 101 degrees C, and is handled as a non-flammable liquid of un regulation.

Table.6 General adhesive property

Item		Low-odor and non-flammable SGA NS700 series		Conventional SGA Our product	
Shrinkage after cure (Vol%)		8.0		13.0	
Adhesive strength	Overlap shear strength, MPa JIS K-6850 cold-rolled steel, oily	20.0		19.0	
	Peel strength by floating-roller kN/m ISO4578(JIS K6854-4), cold-rolled steel, oily	7.0		5.0	
	Impact strength, kJ / m² JIS K-6855 steel, sand blasted	17.0		20.0	
Overlap shear strength MPa JIS K-6850	Stainless steel SUS304(1.5mmt), wipe with paper	22.0	Cohesive failure 100%	21.0	Cohesive failure 80%
	Aluminum A5052P(2.0mmt), sand blasted	18.0	Cohesive failure 100%	19.0	Cohesive failure 70%
	Galvanized steel SECC-P(1.6mmt), wipe with paper	21.0	Cohesive failure 100%	21.0	Cohesive failure 70%

- Low-odor and non-flammable SGA has the character that shrinkage after curing is low. and excellent in the balance of OLS, peel , and impact strength.
- Strength of a SUS, an aluminium, or galvanized steel is balanced, and all are excellent in an adhesive property with cohesive failure.

Stability of bonding strength

Table. 7　Deviation of bond strength / Low-odor and non-flammable SGA

Item	Over lap shear strength SPCC / Oily surface JIS K6850
Number of speciman	50
Average (av.)	21.0
Standard deviation (σ_{n-1})	0.681
Coefficient of variation (σ_{n-1} /av.)	0.033

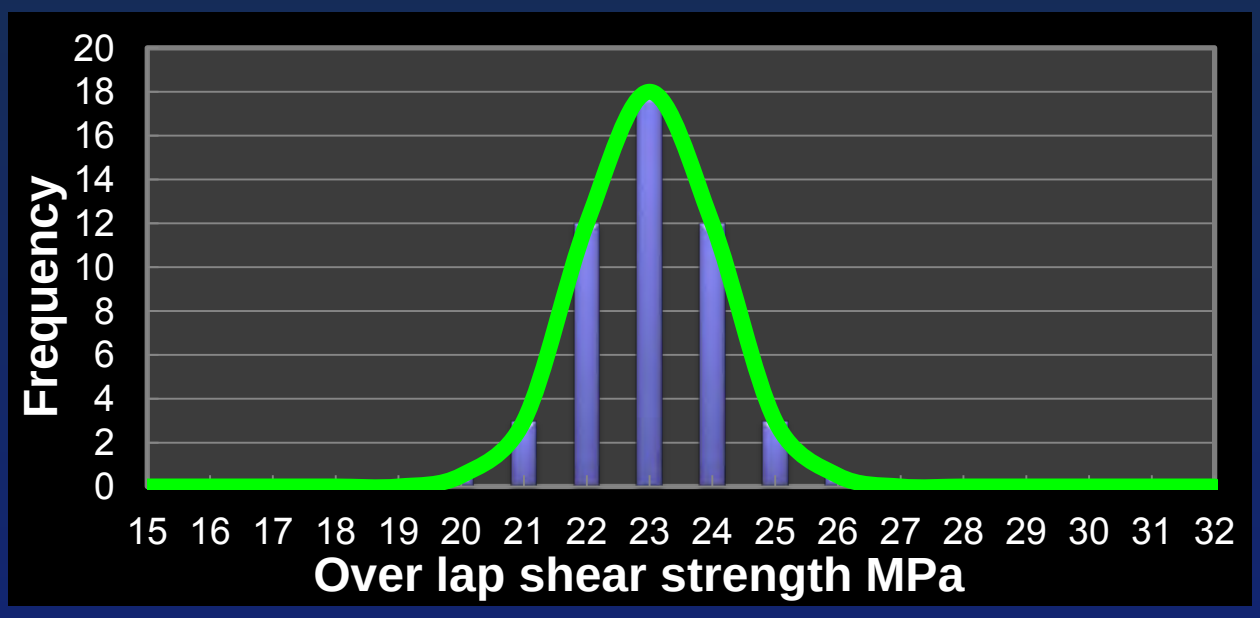


Fig.10　Frequency table of bonding strength

NS700 series
Electrogalvanizing steel / Steel

Fig.11　Cohesive failure (example)

■ **Any material is excellent cohesive failure after fracture, coefficients of variation are 0.033 and the small so and stabilized normal distribution.**

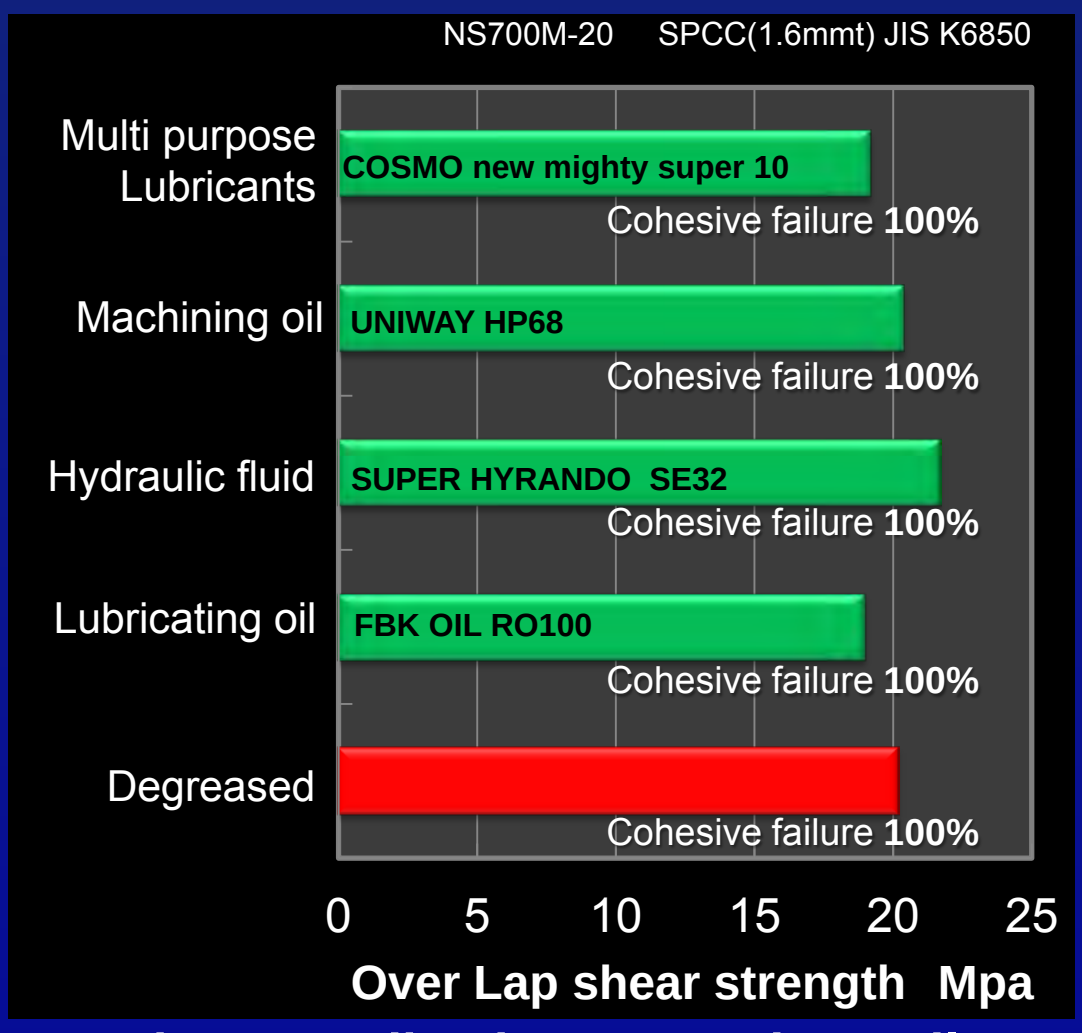


Fig.12　Adhesion strength on oily surface / NS700 series

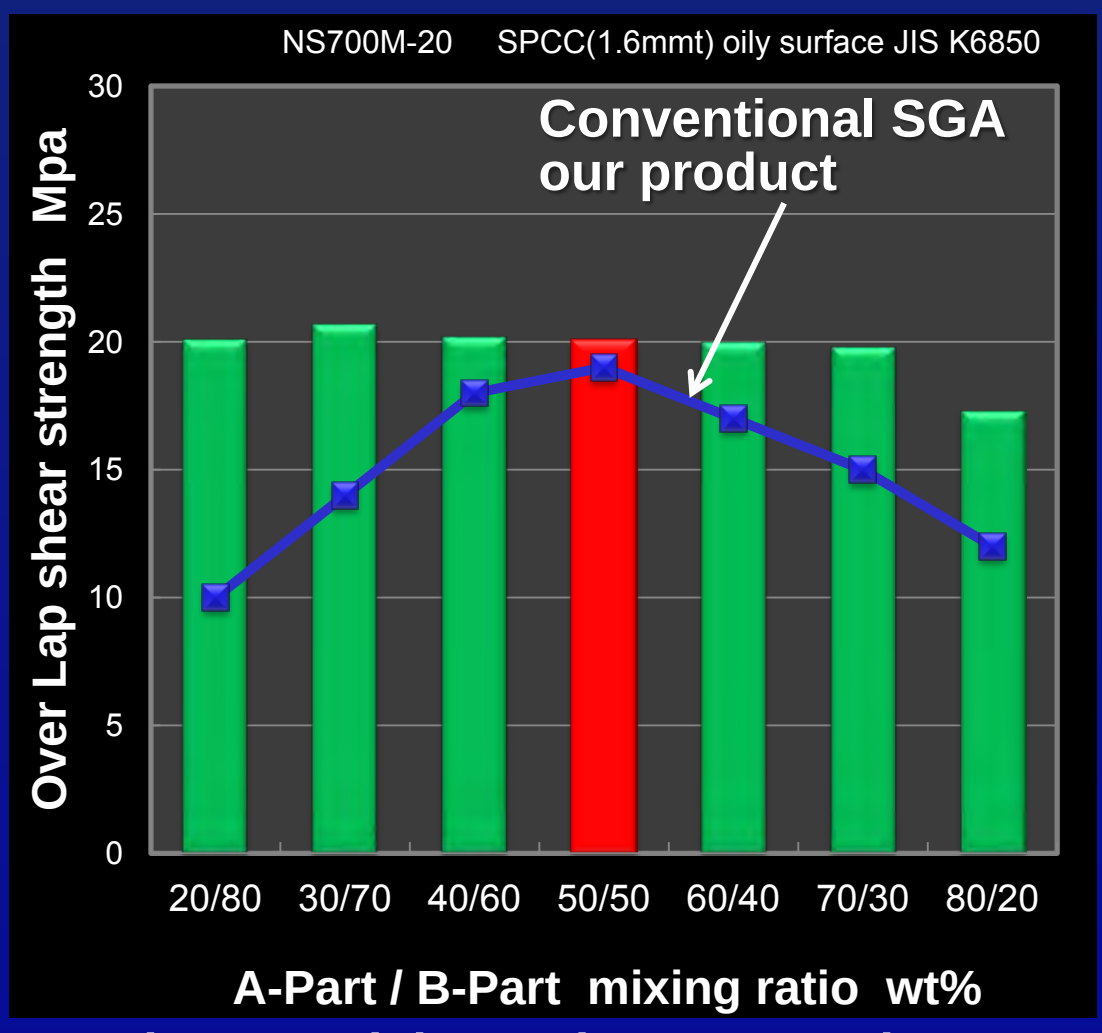


Fig.13　Mixing ratio vs.　Lap shear strength / NS700 series

■ **No strength reduction by the type of oil, and the adhesion performance of an oily surface is very high.　And even if mixed ratios are different, there is little strength reduction.**

Workability

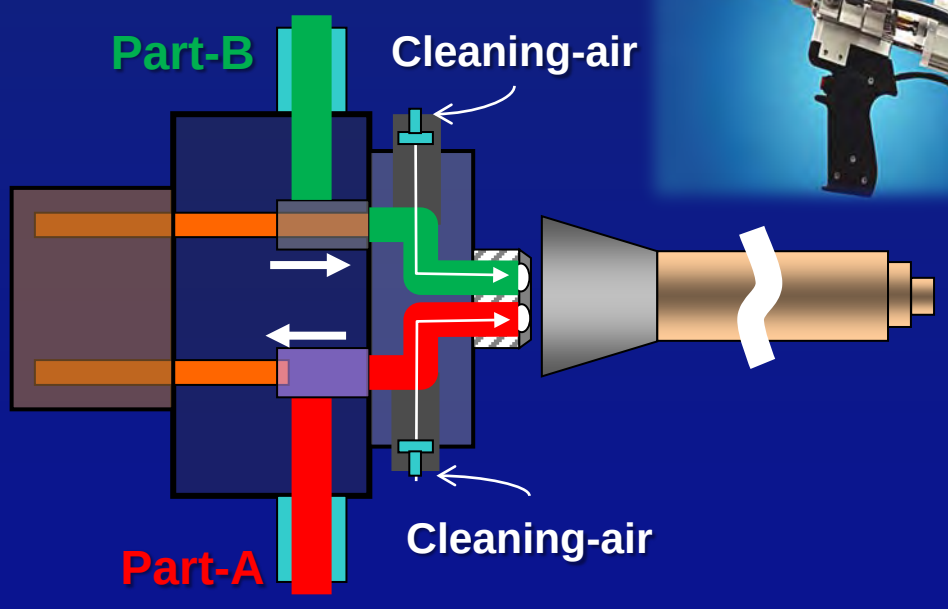
Color change of Low-odor and non-flammable SGA

Table.8 Color tone change in a curing process

Curing process	A-Part	B-Part
Color of A & B	Pale yellow	Dark blue green
Color after mixing	Dark green	
Color after curing	Dark brown gray, With Gloss	Original color, No Gloss

■ Curing process can be confirmed by the tone change of the adhesives originating in a hardening accelerator (Vanadylacetylacetonate).

Automatic air-cleaning application system (AP-5)



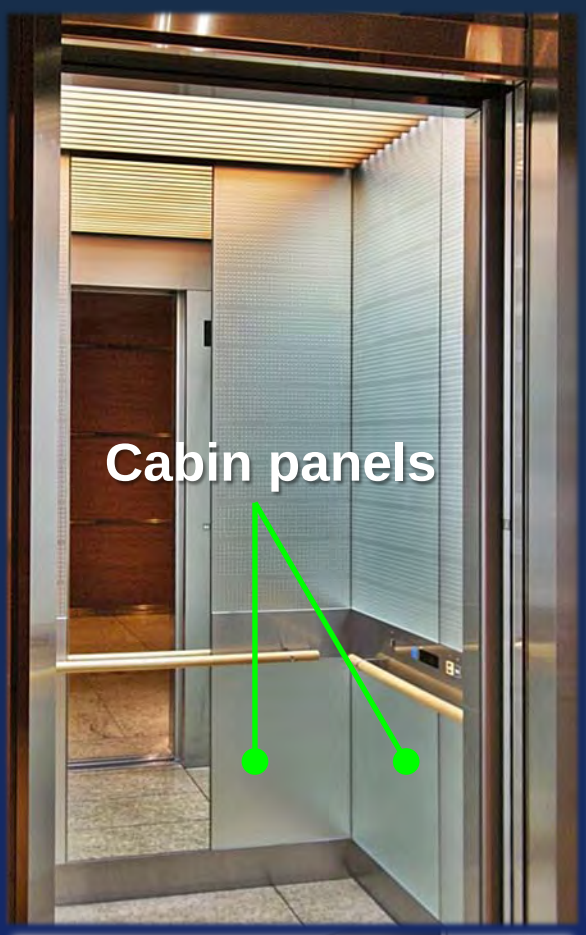
Air-cleaning gun
- Decrease of mixer exchange frequency
- Non use cleaning solvent

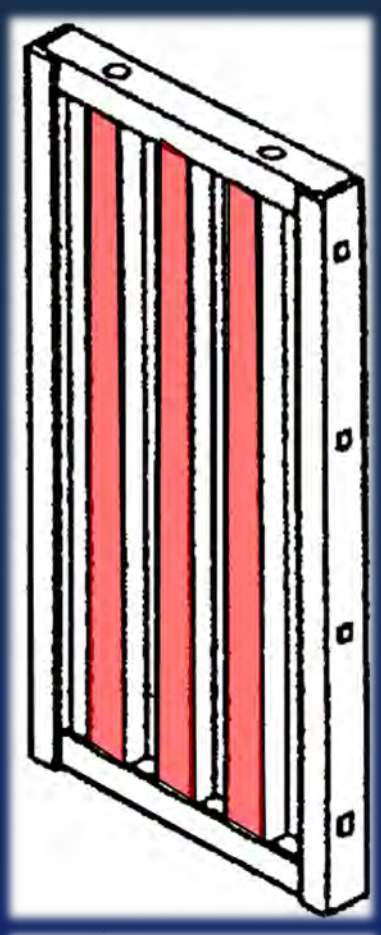
Deodorization system
- Deodorization (by activated carbon)
- Silence (cleaning noise zero)
- Redundant adhesives recovery

Specification	
Discharge pressure	0.5MPa
Discharge capability	20 ml/min-200 ml/min
Viscosity range	3000mPa.s-30000mPa.s
Manufacture / sales	NLC Naka Liquid Control Co., Ltd. URL: http://www.nlc-dis.co.jp

Application cases

Reinforcement bonding of an elevator panel





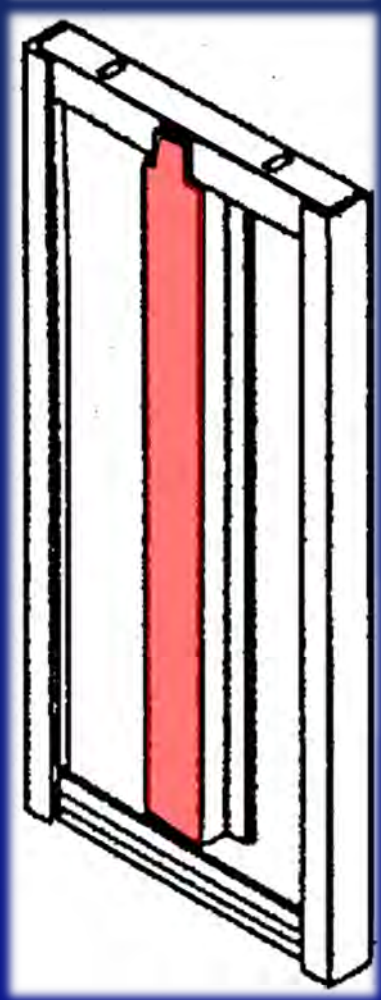


Fig.15 Adhesion of the reinforcement of an elevator panel and a door panel

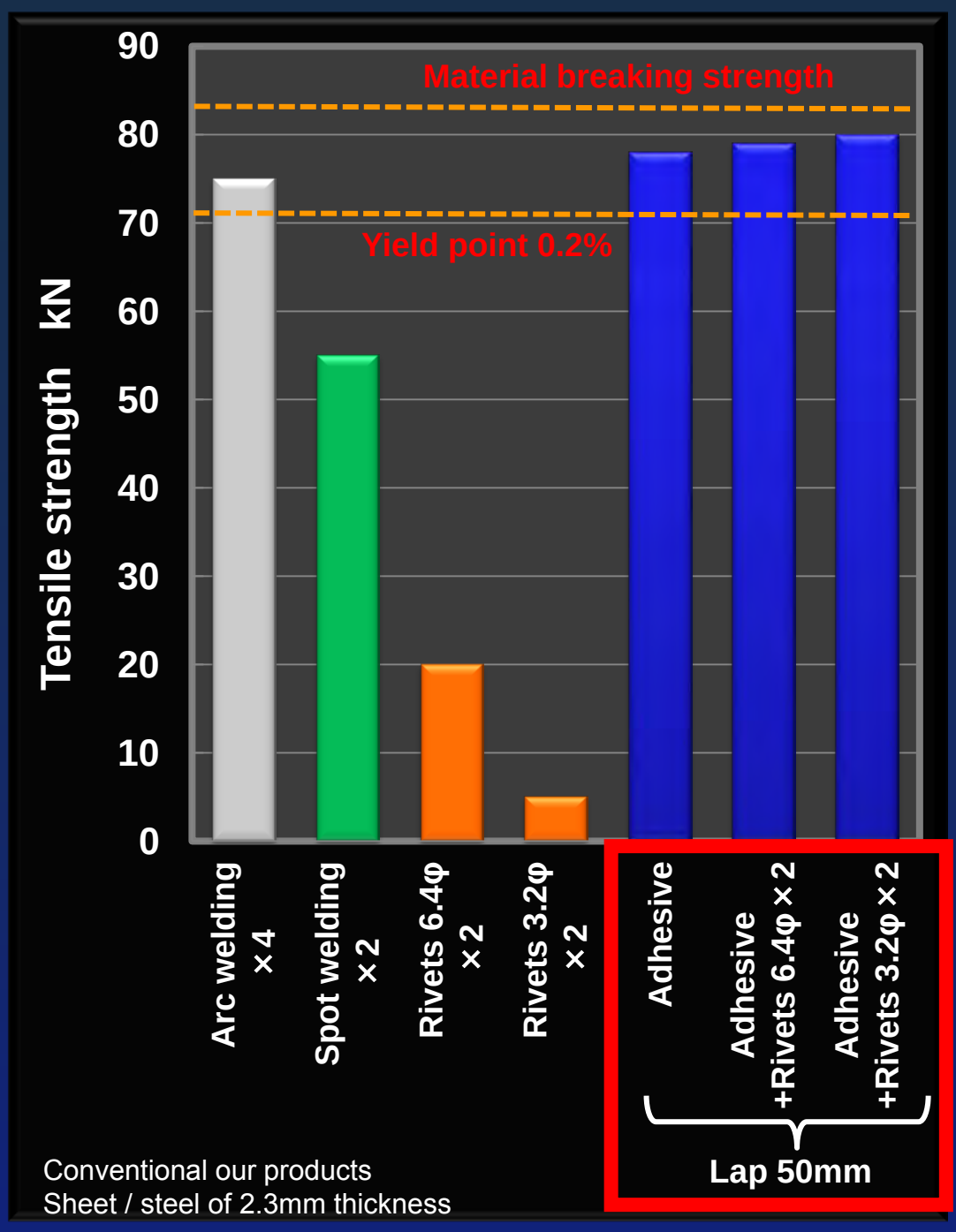
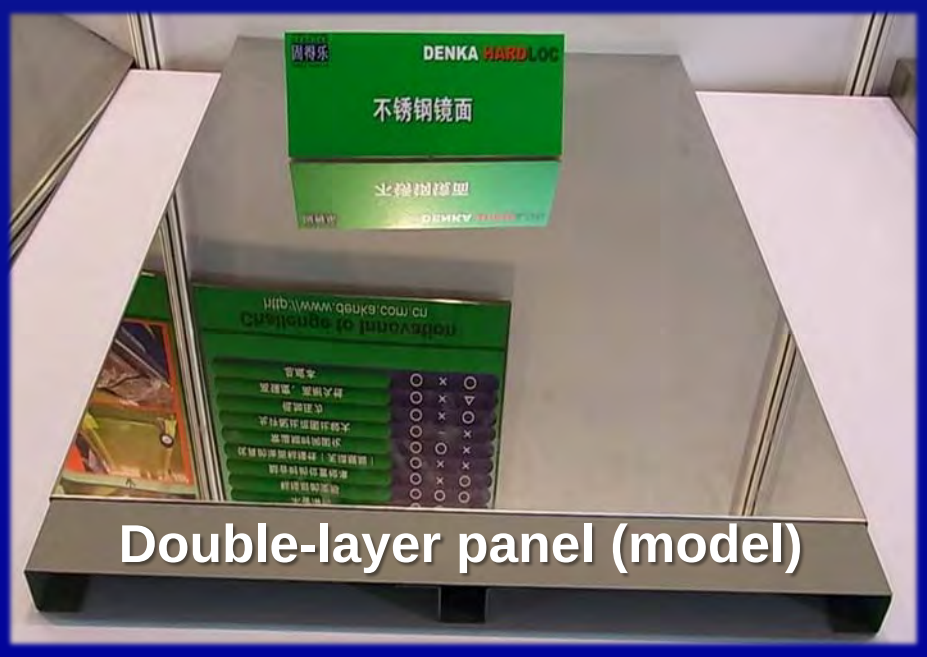


Fig.14 Comparison of the strength of various joints

Fig.16 Valuation modeling (baking painting specification) and valuation method

Manufacture of an elevator double-layer panel



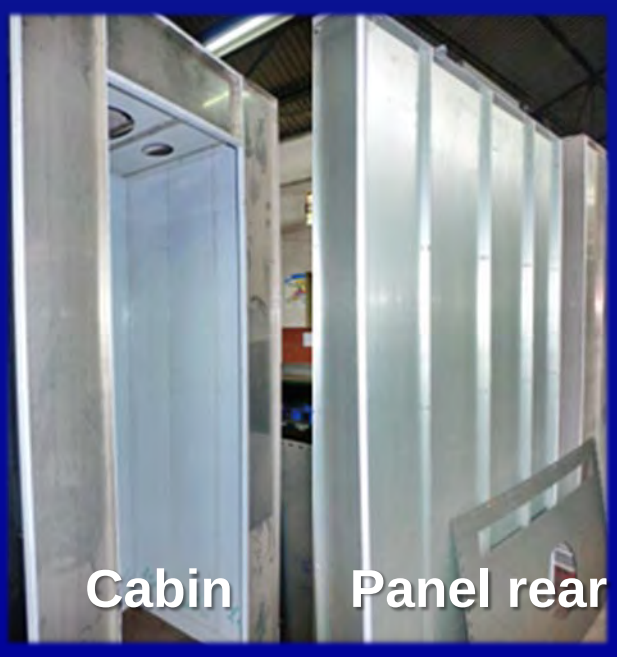


Fig.17
Double-layer panel
(mirror finished SUS)

- Distortion of Low-odor non-flammable SGA which appears in the panel surface is low.

Application cases

Manufacture of the light-weight honeycomb structure

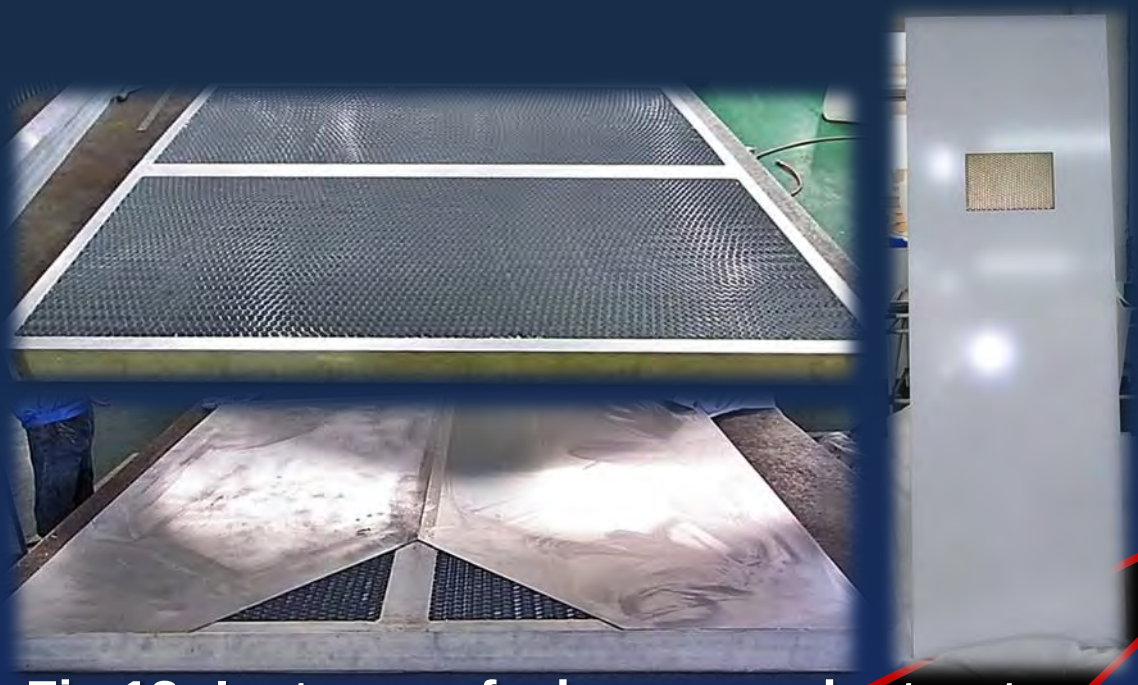


Fig.18 Instance of a honeycomb structure

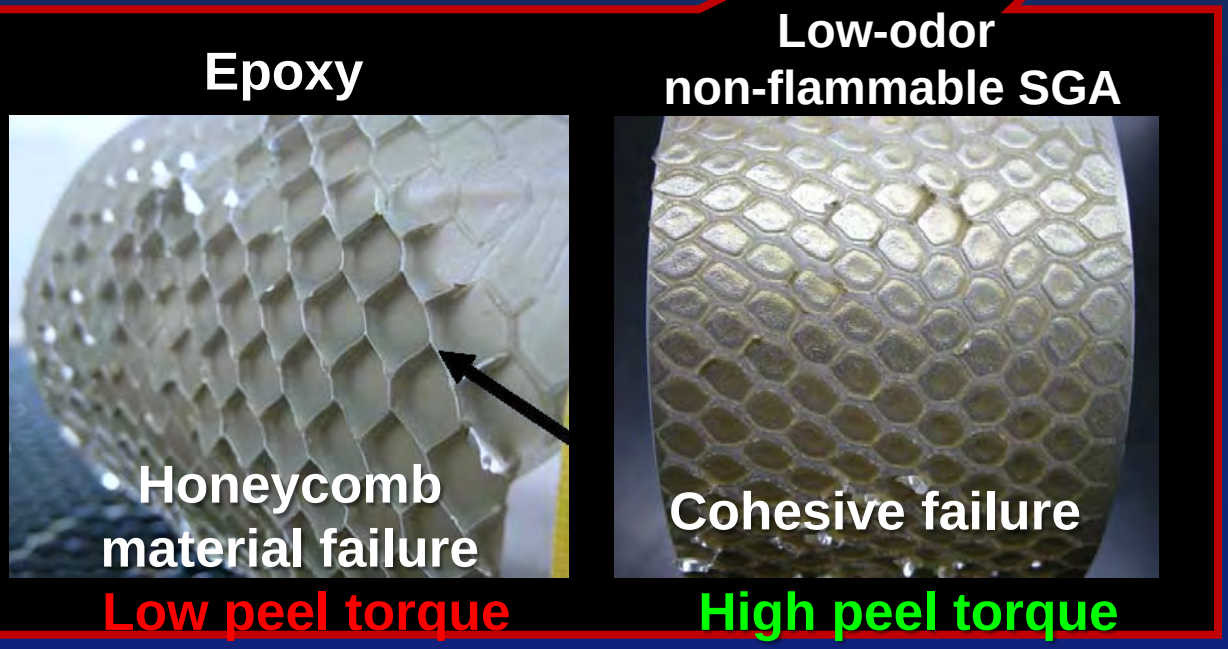


Fig.19 Condition after fracture

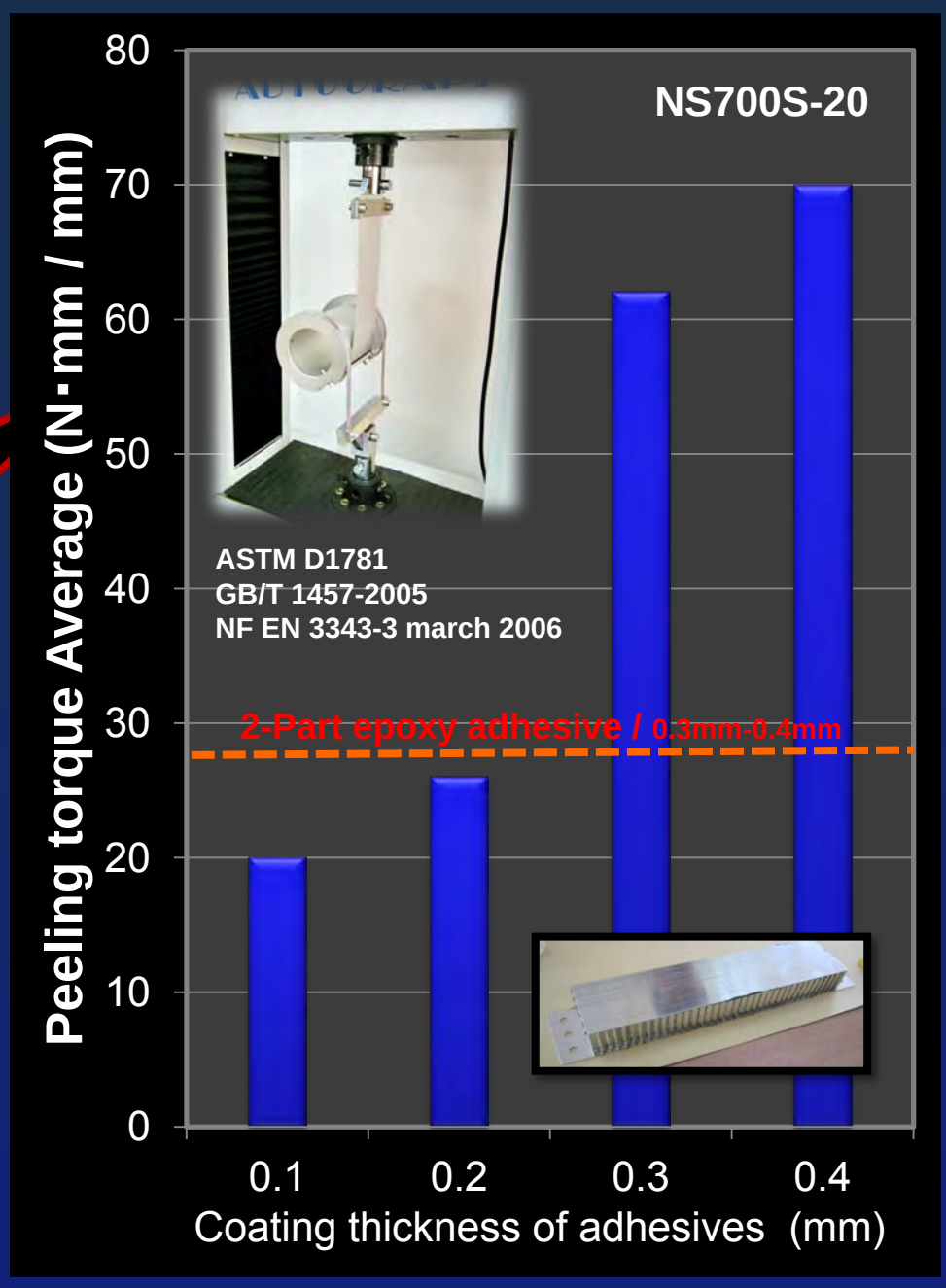


Fig.20 Climbing Drum Peel Test

- Many epoxy adhesives are too rigid and are in the tendency of honeycomb fracture. Accordingly, more than the strength of honeycomb fracture is not got.
- However, a low-odor non-flammable SGA distributes the stress when the fracture compared with an epoxy flexible, and does not cause honeycomb fracture.

Conclusion

In SGA composition, I introduced the monomer with low vapor pressures, such as 2-Hydroxypropyl methacrylate , Phenoxyethyl methacrylate and Acrylic oligomer, instead of the indispensable MMA monomer.
Moreover, We reinforced fracture toughness with elastomer composition, and used Vanadylacetylacetonate as an accelerator.
And we developed a low-odor and non-flammable SGA with the good characteristics of balance.
Furthermore, adhesives are high flash points and 'UN Recommendations on the Transport of Dangerous Goods (CLASS 3-FLAMMABLE LIQUIDS)' is an inapplicable non-flammability liquid.
New adhesives have many characters, such as adhesion on low shrinkage on curing, wide mixing ratio tolerance, and the high surface of an oil, and distinction of the cure process by color change.
Adhesives are used for the assembly of a metal housing, and manufacture of a honeycomb sandwich panel, and the applicability of these adhesives is immeasurable.