AMBITION / FLEXIBILITY / PASSION / INNOVATION

BRB

Silicones for Coatings & Inks

Paint & Coatings

Market Segmentation – Sub Markets

3 market sub-segments

- **Industrial Paints**

  (High and Medium Temp, foul release, Resin Intermediates)

- **Food Release Paint**

  (Bakery trays coating system)

- **Paints Additives**

  (Ind Paints, Leather Coating, Printing Inks, Pigment treatment)

Industrial Paints

Preamble -Basic Glossary

Painting is the act of coating an object for decorative and/or protective purposes and requires:

- A substrate suitable to receive the coating
- A coating suitable for the selected substrate
- An application cycle suitable for a proper coating

Combination of three conditions above allows to get the required performances being purely decorative either protective

First criteria of distinction between coatings is:

Varnish

Binder + Solvent and possibly color.

After drying the coating is transparent. Color is always soluble in the varnish and it must not be confused with a pigment.

Liquid Paint

Binder + Solvent + Pigment+ Filler (optionally) + Additives.

Also existing solventless liquid paints and solids paints (powders)

Preamble - Basic Glossary

Components and functions of a coating are

Binder: base component of a coating; it's a polymer that after drying and/or curing becomes a solid layer bringing adhesion and protection on the substrate.

Solvent: ingredient that allow to apply the coating onto the substrate; as soon as it's made the job it has to evaporate. Possible also to have coating solvent free (solventless or powder)

Pigment: insoluble powder used to make the coating opaque, colored, and mask the substrate. Might also have protective function

Filler: mainly used to improve coverage & impart matte finish.

Additives: used in small amount additives can cover many functions: surface wetting, pigment dispersion, levelling, defoaming, slip, adhesion, texturing, catalyst.

Binders for Industrial Coating

- Binders are the main ingredients of a paint . A binder covers in between 20 to 50% of the total weight of the formulation even more when the paint’s dry.
- Binders impart chemical, mechanical, protective performances and drive the aesthetic of the coating.
- Chemical composition and choice of a binder depends on the final application of a coatings; in the following table a short summary of the most commons binders and related performances.

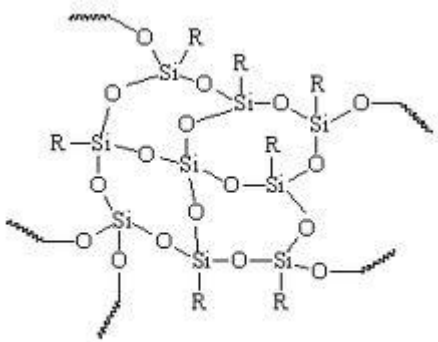
Main Binders for Industrial Coating

Binder	Curing Cond	Aesthetic	Weather Resistance	Chemical resistance	Application
Air Alkyl	Air Oxygen	Good (High gloss)	Medium	Medium	Construction Agro Machinery
Oven Alkyl	In oven (with amino res)	Good	Good	Good	Auto , Tractors met. furniture
Polyester (saturated)	In oven (with amino res)	Excellent	Excellent	Good	Auto, Fridge, Coil
Acrylic (OH, Carboxy, Amido)	In Oven (with amino or expoxy res)	Good/Excellent	Medium/Good	Good/Excellent	Dom Appliance
Epoxy	Amino Catalyst	Medium	Poor crumbling yellowing	Excellent (especially solvents and alkaly)	Protective, Marine
Polyurethanes	Isocyanate react with Polyester OH	Excellent	Good	Excellent	Bodywork, wood furniture
Nitrocellulosic	Physical drying	Good	Medium	Poor	Wood furniture
Vinyl	Physical drying	Good	Good If high thickness	Medium	Protective, Marine
Silicones	Mostly air drying but need to be heat cured	Good	Excellent	Globally good but alkali, some acid, and some solvent when not fully cured	High and Medium Temp, Dielectrical, Protective (top coat)

Silicones Resins

Silicone resins Chemistry

Branched linked caged structures composed of D, T-functional or MQ functional units



- *Durable, thermally stable, UV stable*
- *Various degrees of flexibility and inertness*
- *Enhance weatherability, water repellency, physical strength & release properties*
- *Compatible with a wide range of organics*
- *Solvent-based or solvent-less forms*
- *Can be formulated into aqueous systems*

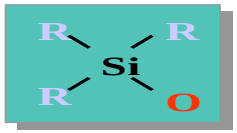
$R_3SiO_{1/2}$ M

$R_2SiO_{2/2}$ D

$RSiO_{3/2}$ T

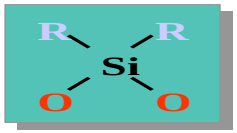
$SiO_{4/2}$ Q

Silicone resins Chemistry



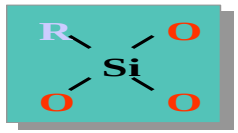
$R_3SiO_{1/2}$

M



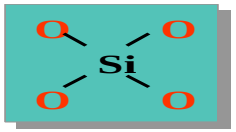
$R_2SiO_{2/2}$

D



$RSiO_{3/2}$

T

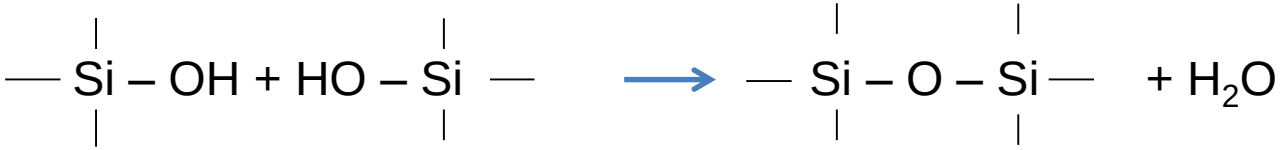


$SiO_{4/2}$

Q

For the most common silicone resins R might be Methyl or Phenyl group.

A resin network has also reactive functions that generally are silanol (-OH) or methoxy (OCH_3) groups needed to build up the network and increase the molecular weight; commercial product as supplied are much more «oligomer/pre-polymer» of low molecular weight; in this status resins don't have the necessary cohesion to act as binder. Once solvent evaporates film start forming by condensation of reactive group below mechanism accordingly:



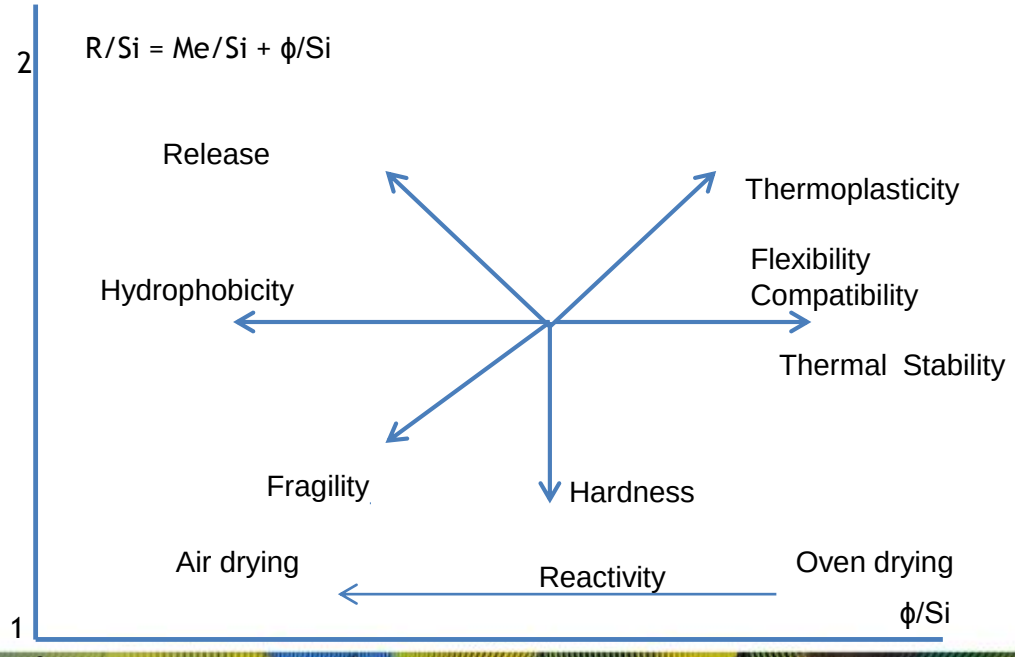
Methyl Groups (Me) bring water repellency, release, incompatibility with organic products, hardness but also fragility

Phenyl Groups (ϕ) bring thermal resistance, Thermoplasticity, flexibility, compatibility with organic products, chemical resistance

Silicone resins Chemistry

Depending on possible blends of functional units, producers can obtain several resins structures. A kind of modelisation useful to understand resins properties (f) of their structure on the diagram below, where on:

- **Y axes R/Si = CH3/Si + ϕ/Si** ratio can range from 1 to 2 and (ratio close to 2 means more linear structure)
- **X axes is the ratio ϕ/Si** ranging from 0 to 1 (typically max one Phenyl group per atom of silicon)



Silicone resins range in aromatic solvent

Product	Type	% solid	Max. Temp(°C)	Application	Resin hardness
BSR SR 379	Me	50	600	Anti corrosion Heat Resistance	Hard
BRB SR 379 N	Me	50	600	Heat resistant Anti corrosion Low viscosity	Hard Bit softer than 379
BRB SR 383	Me, Phe.	50	650	Heat resistant, Anti-corrosion	Medium
BRB SR 313	Me, Phe.	80	650	High Temperature Anti Corrosion High solids Low VOC	Medium

Silicone Alkoxy Oligomer

Product	Type	% solid	Application
BSR SR 833 (ind scale up)	Methyl Alkoxy	100%	Alone as a resin: Room Temperature moisture curing (need catalyst/curing agent) coatings (short tack dry time, high hardness and excellent water-repellency (high temperature paints up to 600-650°C, auto body coating, floor coatings etc) As Organic Resin Modifier (especially Water based) Add typical silicones features (weatherability, Water-repellency, Heat Resistance) to those belonging to organic polymer. Major application: - Acrylic (construction material coatings) - Polyester (industrial, high temp operating appliances) - Epoxy (anti stain, anti corrosive paints) - Alkyd (storage tankers, external structures)

Pigment, Driers, Formulation

Paint formulations

Ingredients selection criteria

- In general we consider heat resistant paints all those paints that must work in continuous service temperature ranging from 200 to 650° C with nor or limited discoloration and no any loss of adhesion.
- Main critieria used to select the most appropriate binder are continuous service temperature and service temperature film hardness. In case of low and medium service temperature paints producers might use hybrid system (silicone - modified organic) where the amount of silicone resin is higher when service temperature increase. Pure Silicones resins system are required for the highest service temperature.

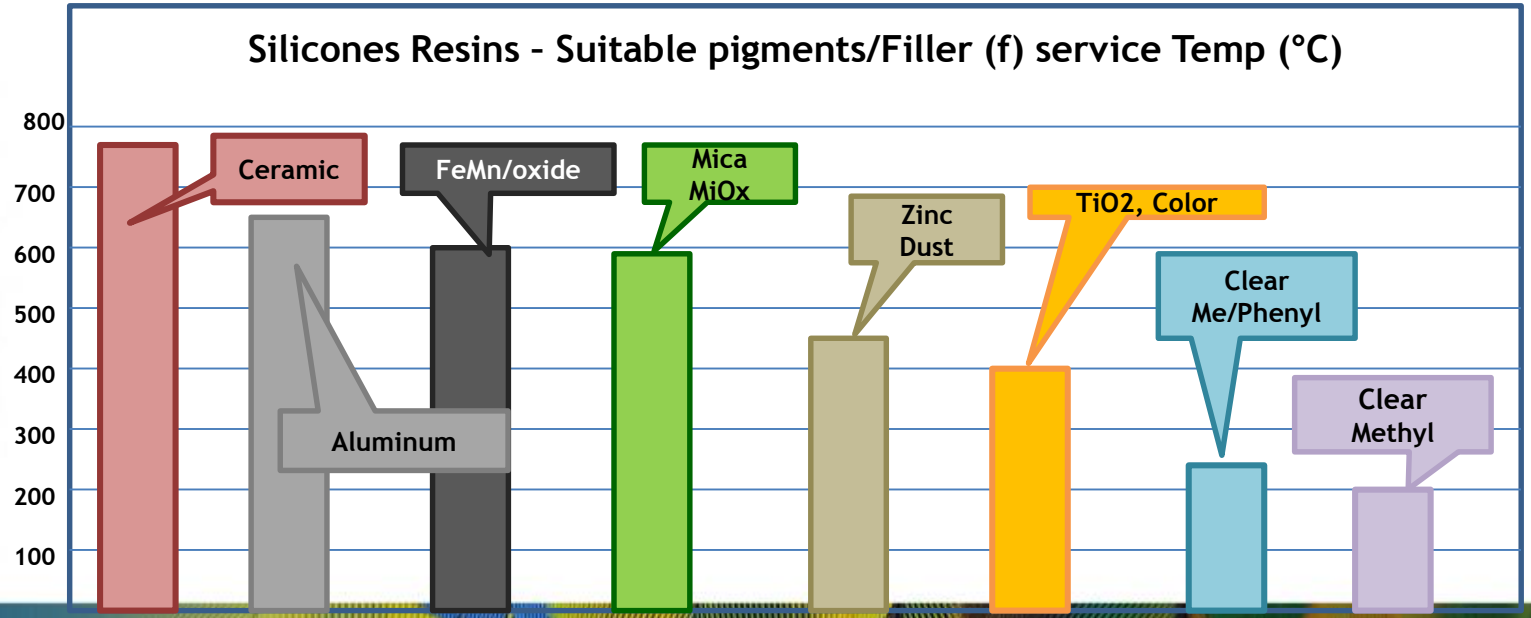
Paint formulations
Ingredients selection criteria

- Softer Silicones resins are typically selected for the highest service temperature whilst harder resins are used for less extreme temperature when hot hardness is required.

- Also pigment will be chosen in functon of the service temperature requirements. Standard colored pigment are generally suitable for formulation not exceeding 350 – 400 °C; for higher temperatures only heat stable pigments should be used; aluminum paste, metal oxides (iron, manganese) and ceramics pigment (see tables next page)

Paint formulations Ingredients selection criteria

Service Temperature	Usueful Binder	Pigment selection
100 – 200 °C	Silicone -modified Organic	All Pigments possible
200 – 320 °C	Silicone- modified Organic	Aluminum Colored Pigment
320 – 420 °C	Silicone or Organic-modified silicones (Sil/Pet –Sil Epoxy)	Colored ,Black,Aluminum, Zinc
420 – 530 °C	Silicone	Colored, Aluminum
530 – 650 °C	Silicone	Black Aluminum
650 to about 750°C	Silicone	Ceramic



Paint formulations

Ingredients selection criteria

- Silicones Resin are thermostable products. When used as varnish their long term (thousand of hours) continuous thermal resistance is about 250°C with no any film degradation. Above 250°C degradation of methyl then of phenyl group progressively start and above 550°C we get a polysilicon layer fully mineral.
- This mechanism is the basic of high temperature resistant paint where in presence of Aluminum paste and Zinc dust (the pigments) a reaction between the polysilicic acid and the metal occur with formation of a polysilicate layer highly cohesive and highly adhesive on the substrate.
- Third party studies demonstrated that despite its volatility, zinc dust is really helpful to enhance the performance of the aluminum

Paint formulations

Ingredients selection criteria

Driers

- To achieve optimum properties silicone paints need to be cured especially when the paint works at very high temperature or when it is submitted to thermal shocks; if resin is under cured film is generally softer with poor adhesion and lower corrosion and chemical resistance.
- Curing, when possible, is achieved through a curing cycle when the paint is heated in between 200°C – 300°C (lower temp for the pure methyl resins – higher temp for the Me/Phenyl resins) for 1 hour. Is typically recommended to increase progressively the curing temperature to avoid blistering.
- Addition of metallic driers (Fe, Zinc, or Cobalt Octoate) improve the cure rate of the paints and reduce their thermoplasticity

Food Release Application

Silicone resins range in aromatic solvent Food Release Application

Product	Type	% solid	Max. Temp(°C)	Application	Resin hardness
BSR SR 385 FD	Me, Ph	50%	300	Non stick Coatings (Bakery Pans , Toaster, BBQs)	Medium

Silicone resins are easier to coat (one step cycle) than silicone elastomers as well as PTFE (multi step process). Number of baking can be extended provided an accurate pre-treatment Re-coating is also less expensive than for the other technologies

Methyl Phenyl Silicones Resins, in general, are not really suitable for high fat-high sugar content products. Silicones Elastomers or PTFE coatings provide better performances in this case.

Additives

BRB - Additive Range (in progress)

Function	BRB Offer	Status
Substrate Wetting	BRB Siloen WA 260	Sample Available
Substrate Wetting	BRB Siloen WA 261	Commercial
Substrate Wetting	BRB Siloen WA 263	Sample Available
Substrate Wetting	BRB Siloen WA 264	Sample Available

BRB - Additive Range (in progress)

Function	BRB Offer	Status
Levelling Flow	BRB Siloen LA 271	Commercial Q1 2017
Slip, Mar Resistance	BRB Siloen SMA 280	Sample Available
Slip, Mar Resistance	BRB Siloen SMA 283	Sample Available
Slip, Mar Resistance	BRB Siloen SMA 284	Sample Available
Slip, Mar Resistance	BRB Siloen SMA 285	Sample Available
Slip, Mar Resistance	BRB Siloen SMA 286	Sample Available

BRB - Additive Range (in progress)

Function	BRB Offer	Status
Defoamer	BRB Siloen DA 290	Sample Available
Texturing Additive	BRB Siloen TA 394 (Hammertone Additive)	Already Commercial former PA 394
Pigment Dispersant (also for plastic appl)	BRB Siloen PDA 222	Sample Available

For more information, please consult the

Paint Additives User Guide

BRB - Additive Range (in progress)

Function	BRB Offer	Status
Adhesion Promoter	Silanil 250	Commercial
Adhesion Promoter	Silanil 919	Commercial
Adhesion Promoter	Silanil 176	Commercial
Adhesion Promoter	Silanil 258	Commercial
Adhesion Promoter	Silanil 581	Commercial

Silanes for Zinc-Rich Coating

Functions of Silanes in Zinc-Rich Coating

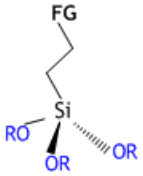
Zinc-rich coating typically contains 60-95% metallic zinc in dry film for purpose of corrosion (cathodic) protection which may be classified into 2 types.

Zinc-rich Coating

Organic Zinc-rich Coating

Silane as Coupling Agent

Silanil 176, 138, 919, 258



http://www.galvanizeit.org

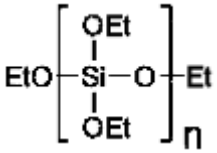
Inorganic Zinc-rich Coating

Based on Alkali Metal Silicate Binders

Silane as Crosslinker
Silanil 118

Based on Alkyl Silicate Binders

Silane as Binder
Silanil 781



I. Organic zinc-rich coating :

Zinc particles are encapsulated by organic binder (waterborne or solvent borne) such as

- > Epoxy-amine
- > Epoxy-polyamide
- > Phenoxy
- > Polyurethane
- > Vinyl
- > Chlorinated rubber

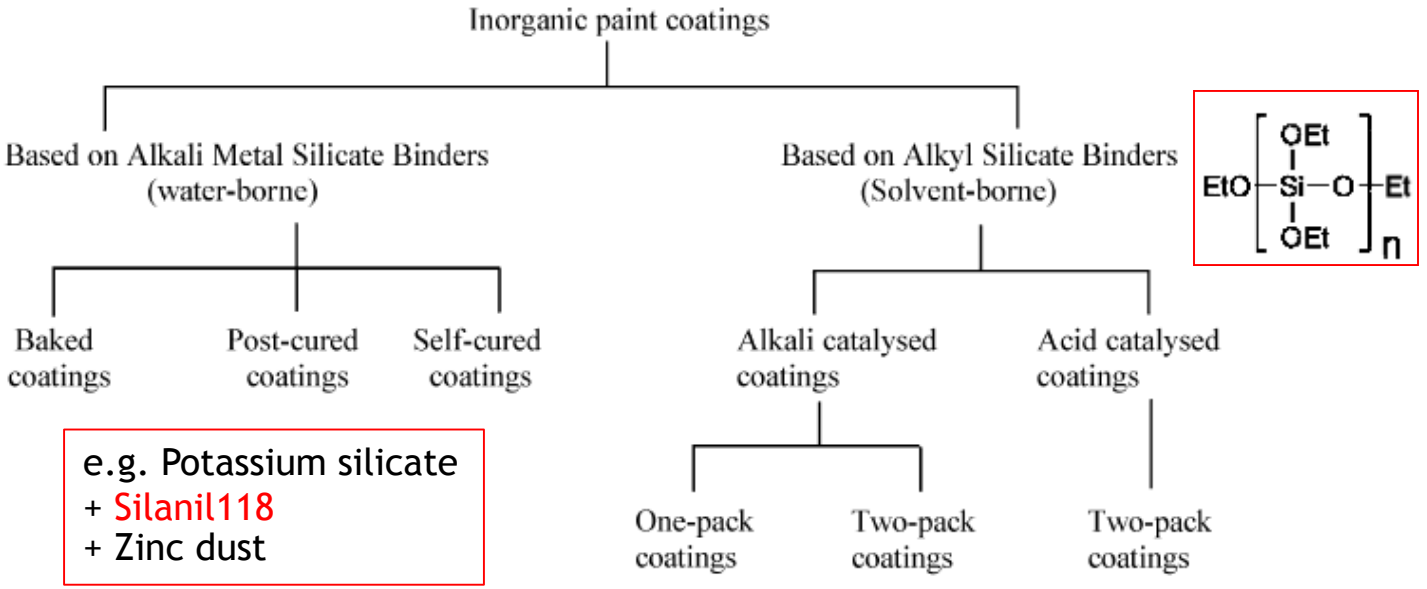
⇧

Silane monomer or oligomer (partially hydrolysed) is post-added in the formulation.

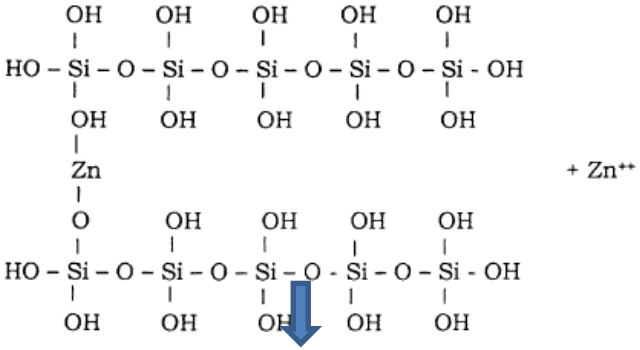
http://www.duluxprotectivecoatings.com.au/

II. Inorganic zinc-rich coating (zinc silicate coating) :

There are 2 types of binders, alkali metal silicate and alkyl silicate. Zinc particles are able to chemically react with these binders and silicate based binder can chemically react with steel substrate.



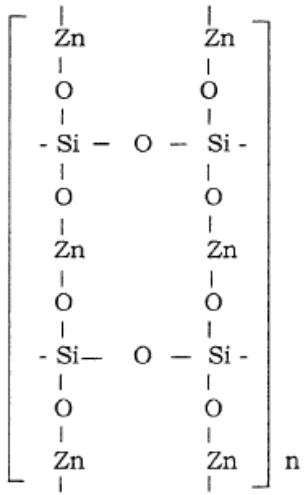
II. Inorganic zinc-rich coating (zinc silicate coating) :



Typical Formulation of Zinc-rich Ethyl Silicate (Silanil 781)

S. No.	Ingredient	Amount (%)
1	Ethyl silicate (partially hydrolysed)	20.0
2	Anti-settling agent (Bentone 38)	1.4
3	Talc	4.0
4	Toluene	5.3
5	Isopropanol	5.3
6	Cellosolve	4.0
7	Zinc dust	60.0
		100.0

"Cured zinc silicate film"



Ref: Parashar, G., Srivastava, D., and Kumar, P. Progress in Organic Coatings *42* (2001) 1-14.

Customer Chain for Zinc-Rich Coating

Resin Manufacturers → **Paint Manufacturers** → **End Product**

- Epoxy
- Polyurethane
- Vinyl

Organic Zinc-rich

Inorganic Zinc-rich

Coupling Agent	Coupling Agent	Crosslinker	Binder
Silanil138,176, 919,258	Silanil138,176, 919,258	Silanil118	Silanil781

Picture Ref. : http://www.galvanizeit.org

Recommendation in Zinc-Rich Coating

Organic zinc-rich coating	Inorganic zinc-rich coating	
	Alkali Metal Silicate	Alkyl Silicate (TES40)
Silanil176 Silanil138 Silanil258 (Up to type of resins)	Silanil 118	Silanil 781 (Si40)

Remarks : Recommendation based on testing and historical experience data.


AMBITION / FLEXIBILITY / PASSION / INNOVATION
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