



Silicones Simplified

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Formulating Tips

Auto Polishes and Tire Dressings

1. Introduction

The word “polish” is a non-specific name but may be defined as any product that enhances and protects the painted surface of an automobile by depositing a thin layer or film of material. More specifically, the name polish is assigned to a product with particular properties, as listed below. Polishes may contain many different ingredients and come in various forms that contribute to a range of final product properties. It is essential to choose the correct ingredients and form to satisfy customers’ needs for specific applications. The following information should assist in making those choices.

Silicones are used to improve a number of auto polish properties, including:

- Ease of application
- Polish cleaning ability
- Ease of buffing
- Gloss
- Color intensity
- Durability and detergent resistance
- Water repellency

The best choice of silicone will depend on the relative importance of the properties above. This is because a polish is essentially a compromise of all the properties.

2. Polish types

Polishes can be described in terms of their physical form, carrier system, ability to clean, and durability. Physical forms of polishes include pastes, pre-softened pastes (non-flowing emulsions), liquids, and gels. There are three types of carrier system:

2.1. Water-free polishes

Where the active ingredients are dissolved in a compatible carrier such as a hydrocarbon solvent.

2.2. Emulsion polishes

Combining two incompatible phases (hydrocarbon solvent + water) by incorporating a surfactant to form a bridge between the two phases.

2.3. Solvent-free polishes

Using pre-emulsified materials with the carrier being water.

The ability of a polish to clean depends on the presence of powders and solvents. Powders clean physically by removing the oxidation layer and smoothing the surface. Solvents clean chemically by dissolving the films and dirt present on the surface. Powder-free polishes, typically referred to as paint conditioners and glazes, are used strictly to provide gloss and protection. They should be applied only to non-oxidized painted surfaces.

A polish may also be described by its level of durability. Durability ranges from temporary (a few weeks) to durable films that remain after numerous detergent washes or months (formerly called “polymer sealants”). To the user, durability is typically judged by a polish’s ability to sustain water beading.

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3. Active ingredients

The term “active ingredient,” as used here, is defined as that part of the polish left behind in the form of a film on the polished surface after application.

3.1 Silicones

A variety of silicones, including polydimethylsiloxanes, aminofunctional silicones, and silicone resins, are used as active ingredients in polish formulations. Silicone emulsifiers, waxes, and volatile silicones are also used in polish formulations and will be addressed in other sections.

Polydimethylsiloxane is a non-reactive linear silicone fluid, which is supplied in a number of viscosities. In the auto polish industry the convention is to classify polydimethylsiloxane as either “intermediate” (350 – 1000 mm²/s) or “high” (above 1000 mm²/s) viscosity.

Intermediate-viscosity polydimethylsiloxanes are lower in molecular weight. They provide excellent application ease and rub-out, as well as streak resistance. Due to their low surface tension, they can improve polish cleaning abilities by increasing the surface wettability. This enables a more direct contact between the powder and the painted surface. They are very good at spreading and thus provide excellent film continuity. The film provided by intermediate-viscosity polydimethylsiloxanes, especially at 1000 mm²/s, provides high shine.

High-viscosity polydimethylsiloxanes are much higher in molecular weight. They provide improvements in durability and provide excellent shine characteristics. However, they are more likely to cause streaking. In general, solvent-in-water polishes use 50 – 1000 mm²/s polydimethylsiloxane, while water-in-solvent polishes enable higher-viscosity polydimethylsiloxanes to be used. In polish formulations it is advantageous to use a combination of high- and intermediate-viscosity fluids favoring the following broad spectrum:

$$\begin{array}{ccc} 3 & : & 1 & : & 1 \\ 350 & 1000 & 12,500 \end{array}$$

This helps to optimize shine and durability in comparison to ease-of-use and film continuity.

Aminofunctional silicone fluids are also used extensively in polishes in both curable (crosslinking) and non-curable forms. They provide properties similar to the polydimethylsiloxanes, but with enhanced durability and detergent resistance, particularly with the curable forms.

One advantage of aminofunctional silicones is that they contain a polar amine group that provides excellent deposition or surface affinity. This effectively anchors the product to the substrate. In the case of the curable amine silicones, a reactive alkoxy group undergoes a condensation reaction that provides a crosslinked film on the substrate. Aminofunctional silicones are available with different viscosities, which allow optimization of properties for a particular application. They are compatible with other silicone fluids and resins and therefore may be blended to create the desired polish performance. Fatty acids may be combined with aminofunctional silicones to improve the corrosion resistance of a polish film. Stearic or lauric acid is often used for this purpose. These can also crosslink with acid waxes through the amino group.

Silicone resins may also be used in polish formulations. These networked silicones are available either bodied or linear and provide intermediate durability to the polish film. When used in conjunction with polydimethylsiloxanes, they provide improved durability with excellent leveling while maintaining similar ease-of-use, shine, and water-repellent characteristics.

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3.2 Waxes

Waxes are commonly found in polish formulations. A wide variety of different waxes are available, including naturally occurring (carnauba), synthetic (silicone wax, polyethylene), and refined (paraffin) waxes. If properly selected, a wax may reduce smear, improve film continuity (or uniformity), provide durability, and promote stability by acting as a thickener.

Most waxes may be described as either soft or hard wax. Hard waxes, such as carnauba and polypropylene, tend to have higher melting points. They provide a harder film finish and promote good gloss, color intensity, and durability. However, they are often more difficult to apply and buff out.

Softer waxes, such as paraffin and beeswax, tend to be better at lubricating, providing better application in terms of rub-out ease and improved spreading. However, soft waxes provide less shine to the system. In most formulations, it is best to blend a hard wax with a soft wax to optimize their benefits in the formulation.

A recent innovation has been the introduction of silicone waxes into auto polishes. These provide a different combination of properties to that of the traditional waxes. While having a low melting point, they can provide a film with increased detergent resistance and weathering abilities, especially when combined with functionalized silicones. They provide a dry film that improves the resistance to dirt pick-up, while retaining the application ease, spreading characteristics, and shine associated with softer waxes.

3.3 Solvents

Solvents are another component of most polish systems and can have an impact on the overall formulation performance. The purpose of the solvent in a polish is to carry the active ingredients; to “wet” the surface so that a uniform film is produced; and to clean the surface. In choosing a solvent, drying rates, combustibility, compatibility with the surface, and compatibility with the packaging must be considered.

It is important to optimize the solvent choice to provide appropriate drying time for the specific application and actives in the formulation. Too little or too much drying time for a specific formulation may lead to poor performance by leaving streaks or a discontinuous film finish. Aliphatic hydrocarbons with Kauri-Butanol values of less than 32 are recommended for polishes. Examples of these include de-aromatized and isoparaffinic solvents. Solvents that contain aromatic substances are not recommended for use in these products because they may damage the surface and may raise flammability, health, and environmental issues.

Volatile silicones are an alternative to these traditional solvents. Volatile silicones provide some unique application properties such as better spreading and lubrication properties due to their lower surface tension, and improved compatibility with silicones. Different evaporation rates can be achieved by blending. This allows even deposition of other ingredients, while their cleaning ability for various deposits is comparable to traditional solvents. It has been shown that volatile silicones do not contribute to tropospheric ozone formation. Therefore, volatile silicones are not classified as VOCs in the USA.

3.4 Powders

Powders or polishing agents provide physical surface preparation and cleaning, and aid leveling of the deposited film. The ability of a powder to clean and smooth out surface imperfections depends on the particle size, its shape, and hardness. The larger and less uniform the powder particle the greater the cleaning ability to remove the oxidized paint layer. Milder powders are composed of more uniform, smaller particles, which polish more and clean less, giving greater gloss. These are better suited to surfaces with little or no oxidation. For cars less than one year old, it may not be necessary to include powders in the formulation. Most powders contain kaolin clays, diatomaceous earths, and hydrated aluminas such as *Sillitin*[®], *Kaopolite*[®], *Diafil*[®], and *Alcan*[®] grades.

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3.5 Emulsifiers

A polish emulsion may be described by either its emulsion system or its ionic character.

An oil-in-water (o/w) emulsion is a system in which the water is the external or continuous phase and the oil is in the form of suspended droplets. These can give a better shine than the other emulsion type, are less flammable and may be considered safer for skin contact.

Water-in-oil (w/o) polishes are popular due to easier processing in some cases and better cleaning properties. Here the oil is the continuous phase, with the water suspended as droplets. Emulsifiers for this type of system have a hydrophilic/hydrophobic balance favoring the oil phase, e.g., silicone emulsifiers. For best results, the water and oil phases are blended separately, and then the water phase is slowly added to the oil phase using a mixer that provides high shear. With some formulations it is possible to blend the phases in a certain order in one vessel.

Silicone emulsifiers represent a unique material for use in water-in-oil polish formulations. These lipophilic materials produce very stable, shear-thickened emulsions. In addition, they are thixotropic, providing excellent application ease. The inherent lubricating nature of the silicone improves rub-out. As emulsifiers they can provide better shine than their organic counterparts due to compatibility with active residual material in the polish film.

Emulsions defined by their ionic character are either anionic, nonionic, or cationic. An anionic emulsion particle shows a net negative charge typical of the formulations, based on the saponification of a fatty acid such as oleic acid and an alkali. Nonionic emulsions show no net charge and are typical of the emulsions, based on alcohol ethoxylates. Cationic emulsion particles have a net positive charge similar to the alkyl quaternary compounds, giving good wetting and substantivity properties as well as synergy with silicones.

The key to making stable polishes is using the right level of emulsifier, correct HLB value, and chemical type for the system – with the ingredients added in the proper order. Oleic acid and a volatile amine can be used together because this combination leaves no residual surfactant on the surface and therefore avoids re-emulsification. Substituting a higher-molecular-weight fatty acid, such as stearic, for the oleic can increase the emulsion viscosity and improve stability.

3.6 Thickeners

A variety of thickeners are commonly used in polish formulations to provide better stability and improved consistency. For maximum efficiency, the external phase should be thickened with no more thickener used than necessary.

In a water-in-oil system, a solvent-based thickener such as bentonite clay can be used. This will increase the viscosity and improve the product consistency as well as reduce the phase separation. The presence of aminofunctional silicones provides a richer, thicker end product with this emulsion type.

With oil-in-water formulations, the aqueous phase may be thickened with natural gums, cellulose gums, or acrylic acid polymers. Magnesium aluminium silicates provide minimum thickening, but tend to reduce powder settlement. This is of particular benefit in spray-and-wipe formulations where lower viscosity is desired.

3.7 Biocides

Microbes can spoil polishes causing breakdown of the product as indicated by a color change or offensive odor. Microbes can also affect the packaging of the polish by distorting the container. Microbial testing must be undertaken to verify whether the product needs protecting.

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3.8 Miscellaneous

Other additives may be added to the polish as desired. For example, coloring agents can be added to shade the polish, while fragrances give an attractive smell. Both are typically incorporated at 0.1 – 0.2% by weight (higher levels of fragrance can affect stability). In other situations the coloring agent (pigment or dye) is added in larger amounts to create “colored polishes.” Other resins, such as acrylic and polyurethane, can be incorporated at low levels to increase the immediate water resistance (not repellency). However, compatibility needs to be determined.

4. Formulation tips

4.1 Stability problems

4.1.1 Oil-in-water polishes

Many different stability problems occur in oil-in-water polishes, but the most common ones can be remedied fairly easily. One such problem occurs when the emulsifying system is the reaction product of a reactive amine source with a fatty acid. If there is interference with this reaction, there will be insufficient surfactant to emulsify the internal phase. It is advisable to combine the reactants in the same phase (usually the oil phase) and allow them to pre-react before adding reactive ingredients such as aminofunctional silicones or neutralizing agents. Problems also occur when the amine content of silicones or other ingredients is too great as this tends to favor water-in-oil emulsions and can actually prevent oil-in-water polishes from forming properly.

If the emulsion forms, but is prone to settling or breaking, thickening the emulsion will often enhance the stability. This may be accomplished by thickening the external phase with gums or acrylic acid polymers.

4.1.2 Water-in-oil polishes

Probably the most common type of instability in water-in-oil polishes is “oiling out” of the phases. This condition occurs because of the natural tendency of the less dense solvents to collect at the top of the polish, but can normally be redispersed by agitation such as shaking. To eliminate this tendency, the emulsion can be made extra thick to reduce the mobility of the phases. Alternatively, steps can be taken to make the phases more compatible, for example by adding a hydrophilic co-surfactant.

Also, applying more shear will reduce the particle size of the emulsion and thicken the polish. It is possible however to over-shear the polish and make the particles too small, consuming the surfactant and contributing to instability. When using silicone emulsifiers, adding 0.5 – 1.0 of a water-soluble electrolyte, such as sodium citrate, in the water phase can substantially enhance stability.

4.2 Performance issues

4.2.1 Streaking problems

Streaking is generally defined as marks or imperfections in the polish film that are immovable, or hard to move, with simple rubbing. In extreme cases streaking appears as harder swirl marks where the polish was originally applied. Generally there are two main causes for streaking:

- The film-forming ingredients cannot level and spread well.
- The film-forming ingredients interfere with each other.

The first cause is usually manifested by insufficient drying time, improper solvent choice, or improper application conditions. Allowing too little or too much drying time can have negative effects on the polish film. It is important to choose appropriate solvents as well as the proper phase ratios (water phase versus oil phase) to provide a drying time that allows the polish active ingredients to wet out to a thin, uniform film.

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Polishes that dry too quickly tend to leave a film that varies in thickness over the surface. This creates a film with poor gloss properties because the actives do not have time to wet out prior to solvent evaporation. This is especially the case for higher-viscosity and reactive silicones.

Polishes that are left to dry for too long may also yield a non-uniform film with poor gloss and color enhancement. This is because after the solvent has evaporated, the remaining actives cannot be buffed to a smooth finish – especially if the materials have begun to crosslink and anchor to the surface. Environmental conditions (primarily temperature and humidity) affect the required drying times; on warm surfaces the solvent evaporates too quickly for reactive polymers to wet out. It is important to consider these factors when choosing the solvent or solvent blend for your formulation. In most cases a polydimethylsiloxane will be more flexible than a reactive polymer, and can accommodate a variety of drying times. If these measures do not eliminate the problem, then a wetting agent should be tried at low dosage levels, typically 0.1 – 0.3%. Silicone polyethers are effective wetting agents used in small quantities; they reduce the tendency to re-emulsify, and avoid incompatibility problems.

The second cause of streaking (i.e., the film-forming ingredients interfering with each other) can be more difficult to resolve. An approach would be to eliminate each ingredient in turn to determine the source of the interference. Sometimes the final film may be compatible, but in getting to that film, there may be stages where ingredients interfere with each other and cause streaking. In this case, choosing coalescing solvents that help solubilize all of the active ingredients can help.

Finally, it must be said that streaking is not an easy problem to solve, so plenty of persistence is required.

4.2.2 Smearing

Smearing is the tendency of a polish film to be too mobile. This can contribute to a more hazy appearance, and show fingerprints or an oily look. Smearing is usually caused by over-deposition of higher-viscosity active ingredients. One solution is to reduce the level of high-viscosity ingredients such as silicones and other materials, or change the ratio of low- and high-viscosity actives. The choice and level of powders can play a significant part in the amount of material left behind on the surface. This can be optimized by trying to incrementally increase or decrease powder and active levels, but this too is a bit of a balancing act and requires perseverance. Every ingredient added or subtracted in a formulation can affect the final properties and physical form of a polish.

4.2.3 Gloss and color

These properties are a function of several factors of a formulation as well as the conditions and surface where it is applied. Gloss can be measured by reflectance properties and clarity of image, while color is assessed from such factors as hue, lightness, and saturation.

“Clarity of image” is how well the finish shows details of the reflected image. A common way to assess clarity is to hold a ruler or printed page perpendicular to the surface of the paint and observe the reflected markings and letters on the paint. This is usually affected by how smooth the surface is. A film-former that is smeary can cause unevenness in the image and can distort the image. However, a film-former that is too rigid, or one that dried too quickly, can cause a spotty or mottled deposition, also resulting in distortion. Clarity can be improved by blending different film-formers; by choosing slower- or faster-drying solvents; or by using a very fine grade of powder to polish the surface to a smooth finish.

Color intensity is often referred to as “jetting” or “wet look” and is influenced by the type of film-former used. Thicker films (e.g., higher-viscosity silicones) will usually help the jetting but this can be carried too far and result in smearing. Hard waxes have the

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same benefits and problems as high-viscosity silicones but have the disadvantage of being difficult to buff. In some instances, where a high level of reactive silicones or hard waxes is used, it is possible for some of the powder residues to be trapped in the film and left on the surface. This reduces the wet look.

4.2.4 Durability versus ease-of-use

Waxes were the first reasonably durable polish components and were applied from solvent over the surface, then buffed to a smooth appearance. The harder the wax the better the durability but the harder it was to buff. Polydimethylsiloxanes were introduced to help lubricate waxes and allowed easier buffing, but these compromised durability. The solution was curable silicones, which allow easy application, spreading, and buffing. They then cure in place and become more durable.

The curable silicones used in automotive polishes are normally aminofunctional ones. The requirement is to apply as much as needed for good durability while retaining good gloss and ease of use. Low-viscosity aminofunctional silicones are more reactive and more durable, but do not provide significant levels of gloss or lubricity. By blending with higher-viscosity aminofunctional silicones or polydimethylsiloxanes, the best balance of durability and ease-of-use can be achieved.

The typical ratio of reactive amino-silicones used in traditional polishes are 4 to 6 parts high viscosity to 1 part lower viscosity. This balance can be adjusted to affect ease of application, buffing, gloss, and durability. Small, incremental changes are best, because altering one property can affect another.

5. Tire care and protectants

Tire dressings, also known as tire renovators, and protectants, also known as vinyl dressings, have the purpose of enhancing the appearance of rubber and plastic surfaces. These products can be water or solvent based. Protectants are typically water-based products. Silicone emulsions made of polydimethylsiloxane fluids can be combined to achieve desired gloss levels. It is recommended to start with emulsions made of intermediate-viscosity fluids and use emulsions made of high-viscosity fluids to improve depth of gloss. Aminofunctional silicone emulsions can be incorporated to impart durability to these products. Notice that some aminofunctional silicone emulsions have cationic surfactants. Choose non-ionic or cationic emulsions when combining with these emulsions.

The recommended silicone actives content for tire dressings and protectants formulations is 15 – 25%.

Silicone polyethers can be utilized to enhance wetting properties for these products. The recommendation is to use 1 – 0.3% depending on how difficult to wet the surface is.

Elastomer emulsions and dispersions, silicone polyethers, and silicone waxes can help to create innovative look and feel finishes such as soft or dry feel. These types of silicones can help to formulate non-oily feel products.

Solvent-based tire dressings can be formulated following the recommended ratios found in section 3.1 (Silicones). The same principles found in polishes on how to achieve different levels of gloss apply to tire dressings.

Product Information

A complete list of XIAMETER® brand fluids is available at www.xiameter.com.

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AGP9787

Form No. 95-706-01

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