Design and development of high-efficient antimist additive (AMA) for high-speed release coating application

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Abstract

Silicone based release coating/liner technology plays a critical role in the pressure sensitive adhesive (PSA) industry and is also heavily used in our daily lives. As a fast-growing 57 billion m^2/yr global market with increasing demand, particularly in the priority consumer and healthcare sectors, the release liner industry is pursuing high-speed production to reduce cost, improve production efficiency and sustainability. The main challenge associated with the high-speed coating production is the heavy mist generation in the coating process. Misting is caused by the high-speed split of thin liquid film during the coating process and increases exponentially with the increase of coater running speed. It is a long-standing/unresolved hygiene, product quality control, and sustainability issue when exceeding 500 m/min coating speed. As a result, heavy misting becomes the biggest challenge towards high-speed coating process which is highly desired by the release coating industry.

In response, a novel patented antimist additive (AMA) technology, produced *via* an innovative and sustainable process and optimized with thorough design of experiments and kinetic studies, was successfully developed by Dow through sound methodology and materials science principles. The new silicone AMA dramatically improves the cohesive strength of the coating formulation, leading to significant reduction of mist generation. The new AMA technology enables the development and commercialization of Dow's next-generation solventless high speed release coating. As a new technology aiming to solve the long-term industrial challenge and establish the next industrial sustainability standard, the new coating successfully removes the major industrial misting roadblock and has superior sustainability features at the same time. The resulting new silicone release coating also delivers unmatched performance compared to best-in-class incumbent technologies. The outstanding coating performance, superior antimisting capability, and sustainable nature of this product, coupled with its food safety, significantly benefit the PSA industry and enables the industry to meet not only the short-term demand surge due to the COVID-19 pandemic, but also the long-term demand growth.

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1. INTRODUCTION

Release coatings are micron thick materials applied and cured onto release liners to provide weak interaction with sticky surfaces and prevent premature and permanent adhesion. There are several types of release coatings, including polyacrylates, carbamates, polyolefins, fluorocarbons, chromium stearate complexes, and silicones. Among them, silicone- or polydialkylsiloxane-based release coatings dominate the market due to their superior performance over other types, such as extra low release force, consistent release performance, chemical & heat resistance, environmental friendliness, *etc*.[1-2] The extraordinary performance are mainly due to the unique chemical structure of silicones, which consists of a strong and freely rotating silicon-oxygen backbone shielded by nonpolar alkyl groups. This unique structure not only results in excellent chemical/heat resistance, but most important gives silicones high chain flexibility, low interfacial interaction and low surface energy, resulting in extra low release force that even surpasses that of Polytetrafluoroethylene (PTFE) with lower surface energy than silicone (silicone: release force: 1 N/m and surface tension: ~22 mN/m vs. PTFE: release force: 22 N/m and surface tension: ~16 mN/m),[3-5] making them ideal for use as release coatings. As a result, they are widely utilized in various areas, particularly in the pressure sensitive adhesive (PSA) sector where they play a critical role of protecting the sticky PSA layer during manufacture, storage, and facilitating easy delamination and label transfer from liners onto the targeted labeling objects. The typical application of release coating includes label application, tape application, hygiene application, *etc*. as shown in Figure 1.

Figure 1. Typical applications of silicone release coatings.

Regarding delivery systems, release coating can be divided into three categories: solvent, emulsion and solventless. Solventless release coating dominates the market (66% market share in 2020)[6] due to many advantages over the other two, such as, extremely low VOC, fast cure, high production efficiency, less soaking and improved sustainability. In terms of cure chemistry, two major types are currently used in the release coating area, including thermal addition cure and UV cure (radical polymerization and ring opening polymerization). Thermal addition cure has established a dominant position in the market due to many advantages over the UV cure, such as fast cure, lower cost, and good release stability.

The release liner industry is a rapidly expanding global market, valued at $57 billion square meter per year,[6] with growing demand particularly in the consumer and healthcare sectors. In response to this demand, the industry has focused on increasing production speed over the past few decades. Higher production speed not only improves efficiency by allowing for increased output per unit of time, but also significantly reduces labor costs and overall energy consumption per unit of product, resulting in lower product costs and improved sustainability. As a result of these efforts, coating speed has increased significantly. In the early 1980s, the typical coating speed used by the release coating industry was 100-200 meters per minute (m/min).[7] However, today's coating speeds can be as fast as 1,600-2,000 m/min. The majority of global laminate manufacturers and their customers have invested in high-speed coaters, and the high-speed coating market share has quickly grown into an important segment of the total release coating market.

The growing market trend towards high-speed coating does not come without consequences. Many technical challenges arise as coating speed increases, including how to achieve: low mist generation as well as the good coating performance, like fast cure performance, good immediate anchorage and aged anchorage performance, total control of release profile, and good release stability. Among them, the biggest challenge is how to suppress the heavy mist generation at high coating speeds to acceptable levels (< 5mg/m^3).[8] Undesirable mist is caused by the high-speed separation of the liquid coating layer on oppositely rotated coater rolls, which increases exponentially with coating speed (Figure 2). Misting is a long term problem in many industries, like adhesive industry, ink industry, paper manufacture industry, release coating industry, *etc*.[9-13] Substantial mist generation not only results in significant down-time to clean equipment from mist deposition, but also causes dusting in the heating oven (loss in energy transfer), significant loss of coating material, potential adhesive contamination, and increased aerosol exposure to workers These drawbacks negatively impact production efficiency, cost, hygiene, and sustainability. Clearly, how to reduce the mist generation to an acceptable level is the biggest challenging technical roadblock which needs to be addressed for high-speed coating industrial implementation. In theory, many routes can be used to efficiently suppress the mist generation at high speed, which will be discussed below. However, strict coating parameters and performance requirements in actual production, along with cost considerations, greatly limit the tools, such as coater modification and line speed reduction, which can be used. A successful high speed coating must meet coating performance requirements as well, such as good coatability, immediate cure performance, immediate/aged anchorage, total control of release force and stable release force profile. Here, a novel antimist additive (AMA) technology and its formulated high-speed coating, which are produced *via* an innovative and sustainable process and optimized with thorough design of experiments and kinetic studies, was reported. This work focuses on solventless release coating system which is predominant in the market.

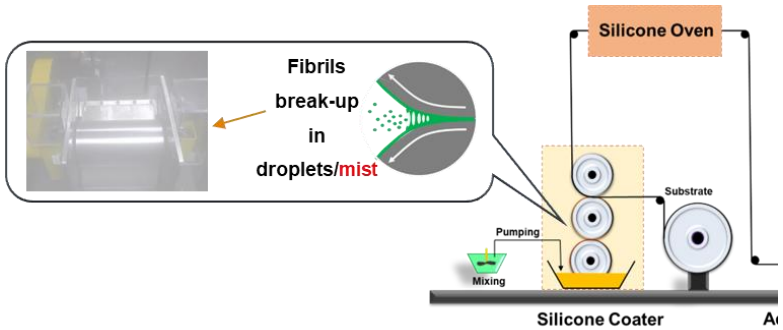


Figure 2. Illustration of mist generation in the high speed coating process.

2. EXPERIMENTAL PROCEDURES

2.1 Materials

All materials discussed in this report are prepared in Dow.

2.2 Characterization and test methods

2.2.1 X-Ray fluorescence (XRF)

The coat weight of silicone coating was characterized *via* X-Ray Fluorescence (XRF) method on Rigaku NEX QC+ QC1499 or QC1747 XRF analyzer.

2.2.2 Mist level evaluation in lab

Mist performance was tested on a custom-designed mist tester coupled with an aerosol monitor Dustrak 8530.

2.2.3 Mist level evaluation on industrial high speed coater

Mist evaluation and cure performance evaluation were conducted on an industrial high speed coater with a 6-roll coating system where the five rollers are in a stacked configuration of alternating chrome steel and rubber sleeved rolls with the first bottom two rolls horizontally aligned together to form a 'nip' where the coating bath is held, and the remaining rolls aligned vertically to allow transfer from one roll to the next until the coating is finally transferred to the paper surface at the 'nip' between the top two rolls. Each of the rolls are pressed together using independent pressure settings and each is driven by a different motor set to a different speed so that there is a stepwise reduction in the coating thickness until the coating is finally applied to the paper surface. A mist collection fixed pipe is located less than 20 cm from the front outside nip of the final 2 coating rollers and is connected to an aerosol monitor Dustrak 8530 (Figure 3). The final top 2 rollers are set to rotate at speeds close to the desired speed, such as 1,000 m/min during the mist evaluation period during which the mist levels are recorded and averaged to be reported as mist values in mg/m^3. The cure performance of the release coating formulations was evaluated by extractable percentage test described below.

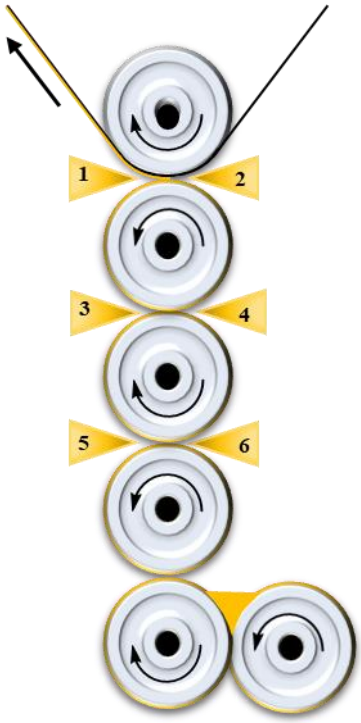


Figure 3. Industrial high speed coater rolls and mist detection location. Front nip 3 were chosen because of the higher mist and easier coordination

2.3.4 Capillary Breakup Extensional Rheometer (CaBER) test

The extensional viscosity of model silicone coating fluids was measured using a Capillary Breakup Extensional Rheometer (CaBER, Thermo Scientific HAAKE). Briefly, a stable liquid bridge of coating fluid is formed between two stainless steel plates after which the filament diameter at the mid-point between the plates (D_{mid}) is recorded as a function of time using a laser micrometer. All samples were tested in triplicate and the filament thinning profiles averaged prior to analysis. The overall filament breakup time (t_f) is determined as the point where the liquid bridge breaks and the diameter is no longer measured. The extensional relaxation time of the fluid (λ_E) is determined from the exponential decay of the filament diameter in the elastocapillary region where $D_{mid} \sim exp\ (-t/3\lambda_E\ )$.

2.3.5 Cure performance: Extractable percentage (extractable%)

Cure performance of a sample composition is evaluated by determining an extractable percent value (extractable %). In particular, a sample composition is coated and cured on a substrate (like Glassine paper) to form a coated substrate, which is immediately cut into three sample discs (die cutter, internal diameter 3.49 cm) handled only by tweezers to minimize contamination and/or damage. Each sample disc is analyzed *via* XRF to determine an initial coat weight (W^i) before being placed in an individual bottle (100-mL, covered with a lid) containing solvent (methyl isobutyl ketone, 40 mL) and allowed to rest on a bench to soak for 30 minutes. Each sample disc is then removed from the bottle, placed coated-side-up on a clean surface (tissue paper) to allow

residual solvent to evaporate (without blotting/wiping), and analyzed *via* XRF to determine a final coat weight (W^f). The extractable % of each sample is the percent change in coat weight from the solvent soak, i.e., is calculated using the formula: $[(W^i-W^f)/W^i] \times 100\%$). The extractable % indicates the amount of non-cured components of the sample composition (e.g. non-crosslinked silicone) extracted from the coated substrate, such as a lower extractable % indicates a higher/better cure performance.

2.3.6 Anchorage performance: Rub-off resistance percentage (ROR%)

The anchorage of a sample composition is evaluated *via* anchorage index, i.e., by determining a percent rub-off resistance (ROR%) value. In particular, a sample composition is coated and cured on a substrate (Glassine paper) to form a coated substrate. The resulting liner is tested immediately or aged for a certain period of time before testing. The liner is cut into two sample discs (die cutter, internal diameter 3.49 cm), which are each analyzed *via* XRF to determine an initial coat weight (W^i). Each sample disc is then abraded with a felt under a load (1.9 kg) using an automated abrading equipment, in a method similar to a Taber-type abrasion test (e.g. such as that of ASTM D4060-19, "Standard Test Method for Abrasion Resistance of Organic Coatings by the Taber Abraser"), and subsequently analyzed *via* XRF to determine a final coat weight (W^f). The ROR% of each sample is calculated using the formula: $[W^i/W^f] \times 100\%$). The ROR% indicates how strong the coating is anchored to the substrate, such that a higher ROR% indicates a higher/better anchorage.

2.3.7 Release test

The release liner sheet was laminated with tape sheets. The laminated sheets were aged under weight ($20g/cm^2$) in a controlled temperature and humidity room (23 °C/50% relative humidity) for certain time. Then, the laminated sheets were cut into strips. Strips were tested on IMASS ZPE-1100W at medium to high delamination speed (10, 100, 300 m/min), and tested on IMASS SP-2100 slip/peel tester at low delamination speed (0.3 m/min). 180° degree peeling method was used. Each sample was tested in triplicate.

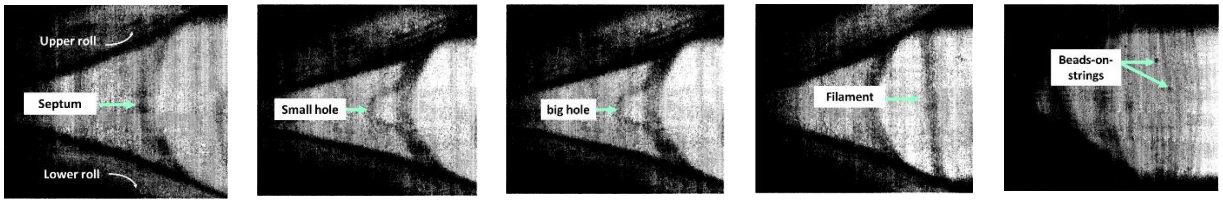
3. RESULTS AND DISCUSSION

3.1 Misting mechanism

As previously mentioned, the release coating industry is striving to achieve high-speed coating production. However, one of the major challenges they face is the significant amount of mist generated during the coating process. To address this issue, it is essential to gain a deeper understanding of the mist generation mechanism. Although misting is a well-known problem in coating processes, there is still much to be learned about the mist generation of silicone solventless release coatings. Despite 40 patents filed from 2000 to 2017 related to this mist issue, there is limited fundamental knowledge available in the literature.

One of the primary reasons for this knowledge gap is the technical challenges involved in observing and monitoring high-speed coating processes in real-time. The variety of coating techniques and materials used also presents a challenge to researchers seeking to gain a better

understanding of mist generation. Later, high speed imaging became a capable tool to explore the misting process.[14] Owens, *et al.* used high-speed camera technology to monitor the mist generation process of Newtonian and non-Newtonian liquids, including PDMS, between rolls rotating in opposite directions at relatively high speeds (up to 306 m/min).[10-12, 14] Although the tested speed was still lower than what is considered high speed today and mist generation is typically minimal at such speeds, the study offers valuable insights into the understanding of mist formation and can aid in the development of new anti-mist technologies. Viitaniemi further investigated misting and coating performance of several solventless silicone release coating formulations to understand the relationship between structure and performance.[15] However, the study does not provide key information such as line speeds and polymer structure. In both works, the polydimethylsiloxanes (PDMSs) were considered as Newtonian liquid. However, the small coating gap in-between the rolls and the large line speed, like 1,000 m/min, results in very high shear rates > 10^6 s^{-1} under which even the linear PDMSs with relatively low viscosity are unlikely to maintain the Newtonian liquid behavior.[16] In terms of non-Newtonian liquid, Owens *et al.* discovered the formation of mist can be divided into five stages as shown in Figure 4: a. A liquid septum is formed at zero reference time. b. The space at the nip dynamically increases beyond possible expansion of the septum shortly generating an air gap behind the meniscus front line. This air pocket (hole) formation is also promoted through air suction from the back of the nip by deformation of the bottom rubbery coated roll dilatation due to high compression shear rate *vs.* undeformed stainless-steel upper roll; c. The hole grows behind the meniscus due to visco-elastic mismatch between the liquid septum and the ever-increasing gap to be filled provoked by the rotating rolls; d. The growing hole reaches rolls surface releasing a filament; e. Series of filaments and beads-on-string are formed which beyond elongation, break-up into a multitude of liquid droplets ejected as mist particles.[10, 12] Although a poly(ethylene oxide) (PEO) solution was studied and the test speed (up to 306 m/min) was far below the current high speed coating definition, this process still can be used to describe the mist generation of the typical release coating polydimethylsiloxane (PDMS) liquid which demonstrated non-Newtonian behavior under high shear rate.



a. Formation of a liquid septum at zero reference time

b. Septum meniscus elongation generating a hole (0.17ms)

c. Hole grows due to stretching by the coater rolls (0.83 ms)

d. Growing hole reached roll surface forming filaments (1.0 ms)

e. Filaments snap and drops are ejected as mist particles

Figure 4. High speed image showing mist formation process in a polyethylene oxide (PEO) glycerol/water solution. Reproduced with permission from reference[10].

3.2 Solventless release coating mist impacting factors

There are various methods to reduce silicone misting generation during the coating process, which can be broadly categorized into two main approaches: modifications to the coater and coating process, and modifications to the coating characteristics.

The first main approach to reducing silicone misting during the coating process is through coater and coating process modifications. One effective method is to use a coating method that can minimize misting, such as a slot die coater or reverse roll coater. However, the relatively expensive and complex roll coaters, such as 3-roll gravure coaters and multi-roll coaters (Figure 5), are required to coat solventless release coatings to achieve the desired low coat weight (0.3-1.2 g/m^2), coating thickness (~1 μm), and high production efficiency. Moreover, the high cost associated with changing and modifying coating equipment is often not feasible for the industry.

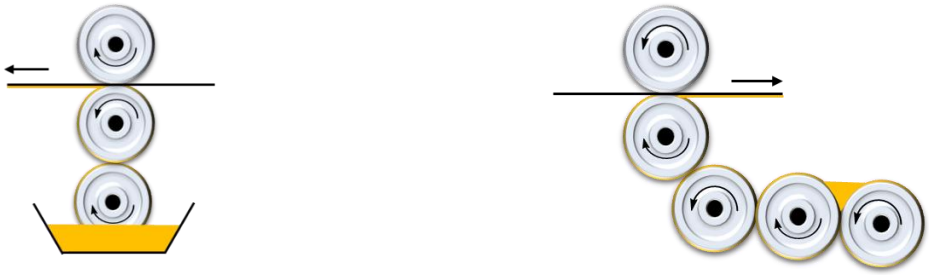


Figure 5. 3-roll offset gravure coater (left) and multi roll coater (right). Gravure coaters use an etched cylinder to apply the silicone coating to the surface.

Aside from the type of coater used, other coater and coating process parameters also affect mist generation. Firstly, line speed is the primary factor. The faster the line speed is, the heavier the misting is (Figure 6). However, reducing mist generation by lowering the line speed is not acceptable for production efficiency. Secondly, roll diameter also impacts mist generation. Increasing roll diameter leads to lower misting levels,[10, 17] ascribed to the slower liquid separation rate and lower septum shear stress on large coater rolls than on small coater rolls when the same line speed is used. Thirdly, coater roll speed ratio (the roll velocities of adjacent rolls rotating in the same direction) affects mist level. A high roll speed ratio suppresses fluctuations in septum thickness and leads to a lower mist level, but this is not achievable at high coating speeds. Fourthly, coat weight affects mist level. Higher coat weight results in lower mist level (Figure 6), which was ascribed to the decrease in rupture of the liquid film and formation of mist droplets with increasing coat weight.[18] However, in real industrial applications, coat weight is determined by downstream applications, and the variation range is limited, making coat weight control a less effective tool for mitigating mist generation. Other factors such as nip impressions, roll temperature, and roll surface condition also affect mist generation. In summary, mist reduction can be achieved through changing the coating method, modifying the coater, and adjusting coating running conditions. However, most of these methods are not feasible from the downstream application perspective due to many disadvantages associated with them, like high cost, low production efficiency, and poor product quality.

In addition, mechanical methods can also be utilized to passively reduce mist concentration around the coating head, thereby limiting worker exposure to mist and slipping hazards caused by slippery floors. There are two major methods that can be used: extraction and enclosure. With the former, exhaust tubes or channels can be placed close to the coater rolls to move the generated mist through a filter to another location. While this method does not reduce the mist, it displaces the mist away from the operators' zone. However, the filter can become quickly clogged, and significant material

loss caused by misting cannot be avoided *via* this method. Thus, it is not the optimum method and is often used in conjunction with other methods to reduce EHS concerns. With the latter, the entire coating head is enclosed in a box to limit the mist generation within a defined area. However, the enclosed area is inevitably coated with silicone, leading to silicone coating loss and liner backside contamination. Both approaches are used to limit the negative impact of misting but does not solve the misting issue.

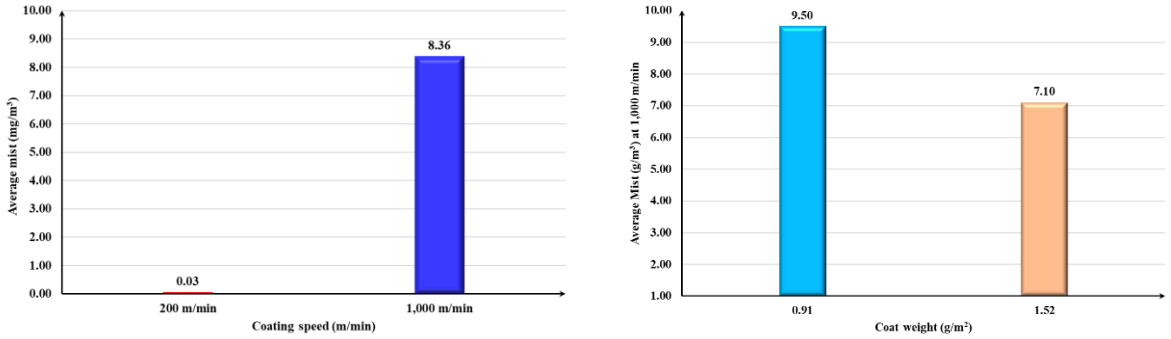


Figure 6. Impact of coating speed and coat weight on mist generation. Left: Average mist level of a model solventless release coating A at two coating speed of 1,000 and 200 m/min respectively. Right: Average mist level of a model solventless release coating B with coat weight of 0.91 and 1.52 g/m^3 at 1,000 m/min coating speed

The second category focuses on modifying coating characteristics, such as molecular architecture, viscoelastic properties, and interfacial properties, to achieve low misting. Solventless release coatings based on thermal addition cure typically consists of four key components: a. polymer bearing unsaturated bonds, b. SiH functionalized crosslinker, c. inhibitor (e.g. alkenes or alkynes), and d. catalyst such as platinum or rhodium catalyst. The polymer and the crosslinker typically represent 80 and 20 wt% respectively of the total coating bath. Therefore, changing the characteristics of the polymer and crosslinker can be an effective way to minimize mist generation. Reducing viscosity and increasing surface tension, have been claimed as effective ways to mitigate the misting issue.[10, 15] However, the selection of polymer and crosslinker systems is primarily dictated by the coatability and performance of the coating, such as cure performance, immediate and aged anchorage performance, release force control, and release stability. The typical viscosity range of release coating is 100-500 cPs. Changing the viscosity of the polymer inevitably affects coatability by impacting the silicone transfer from roll to roll/substrate and the wetting of the coating on the substrate. Within the typical release coating viscosity range, the mist generation of polymer, even with low viscosity, is still far above the desired industrial threshold of 5 mg/m^3 at 1,000 m/min, as shown in Table 1. In terms of surface tension, a relatively significant change in the surface tension of PDMS is required to show a noticeable impact on mist reduction. However, this means that a relatively large amount of polar groups must be incorporated into the PDMS, which can negatively impact one of the key parameters of release coating, namely release force performance, and may not be practical. Therefore, modification of polymer or catalyst characteristics can be an option, but not a perfect solution.

Table 1. Mist level of same type silicone polymers with different degree of molecular weight (Mw) and viscosity.

	Polymer Viscosity (cPs) at 25˚C	Mw (Da)	Average mist at 1000 m/min (mg/m3)
Silicone polymer	259.8	16,644	175.34
	175.8	12,294	141.50
	140.6	11,353	115.29

The most practical way to reduce mist generation is by adding a small amount of additives (usually 1-2 wt%) to the coating to change its characteristics and reduce misting (Figure 7). These additives are commonly referred to as antimist additives (AMA) in the release coating industry. The first generation of these additives was introduced in 1995 by Dow Corning (now Dow Silicone Corporation), which significantly reduced the amount of mist generated. However, negative impacts on coating performance were observed in real-world applications. Thus, second and third-generation AMAs were developed in the early 2000s and 2010s to solve the problems with the first generation and further improve mist control. The third-generation AMAs are capable of reducing mist at line speeds lower than 500-600 m/min, but their performance is not good enough at higher line speeds. Therefore, the development of new AMA technology and resulting high-speed coating is of great significance in meeting the strong demand for high-speed release coating from the PSA industry.

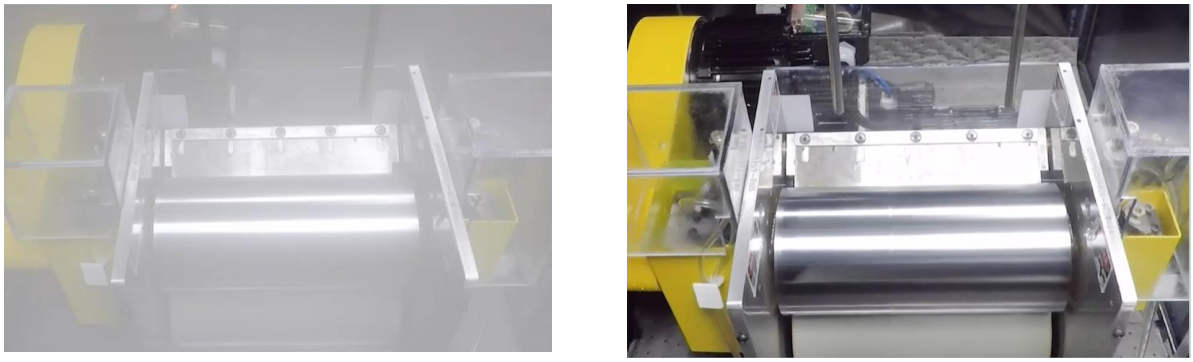


Figure 7. The misting of coating with and without AMA (left: formulation without AMA, Right: formulation with the Dow's 4th generation AMA) at 1,300 m/min line speed.

3.3 Design and development of new antimist additives (AMAs)

To develop a new AMA, along with mist suppression ability, other criteria should be considered in the development of new AMAs, including: a. No EHS concerns, low VOC, and compliance with indirect food contact recommendations; b. Compatibility with existing silicone release coating systems, without phase separation or side reactions; c. No negative impact on coating performance, such as coatability, cure performance, anchorage performance, release performance, and stability.

Based on the above considerations, a new silicone AMA prototype (AP) - AP 1, was designed and prepared. The design was based on prior art analysis, a thorough understanding of mist mechanisms, and Dow's expertise in material and analytical sciences. To ensure compatibility with other components of the silicone solventless release coating system and to avoid negative impacts

on release performance, the AP-1 mainly consists of dimethyl siloxane units which have excellent compatibility with polydialkylsiloxanes without the aid of solvent. Small amounts of functional groups were incorporated to prevent cure and silicone migration issues. In addition, an innovative solventless route was used to produce the AP-1, which included a thorough design of experiments and kinetic studies to greatly improve process sustainability. After preparation, AP-1 was formulated into the same model coating system (Coating 1) and tested at 1,000 m/min. A custom-built 2-roll mist tester was used to quantify mist generation under conditions similar to those in industrial coating processes. As depicted in Figure 8, the mist level is 175.34 mg/m^3 without any AMA, far exceeding the industry targeted threshold of 5.00 mg/m^3. Adding the incumbent 3rd generation AMA from Dow dramatically reduced the mist level to 8.59 mg/m^3, which is still above the threshold. However, incorporating the new AP-1 into the model coating at the same level resulted in a dramatically-reduced mist level of only 2.00 mg/m^3, much lower than the incumbent AMA and the 5.00 mg/m^3 threshold. Clearly, AP-1 is superior to the incumbent AMA and can suppress mist generation at high speeds below the threshold.

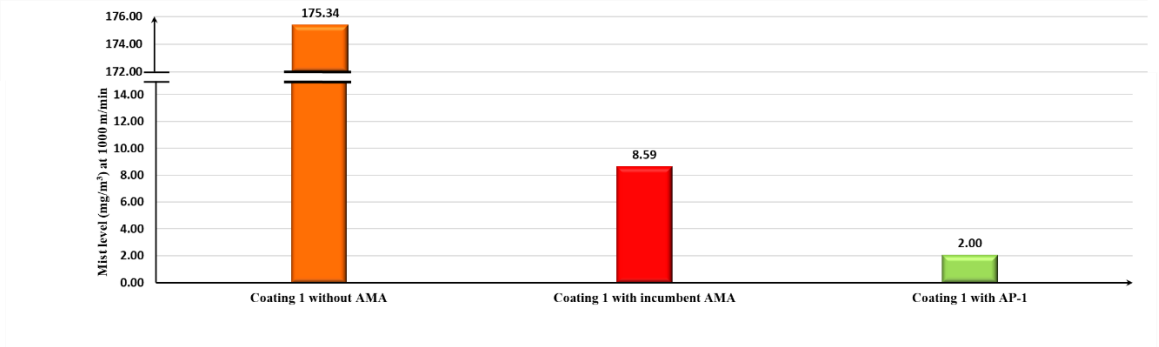


Figure 8. Mist reduction performance of Coating 1 without AMA, with incumbent AMA and with new AMA – AP-1 at 1000 m/min.

As shown by *Owens et al.,* (Figure 4), liquid septa that form at the nip between two rollers undergo rapid stretching and mist is generated as these strands breakup and form droplets that eject from the coater. The process of forming and breaking liquid strands thus subjects the fluid to a predominantly extensional deformation. We performed Capillary Breakup Extensional Rheology (CaBER) to understand how the fluid rheology is impacted by the presence of the new AMA additive.

The coating fluids from Figure 8 were tested in CaBER and the results shown in Figure 9. The filament thinning profiles (D_{mid} vs time) demonstrate that coating with AP-1 have longer-lived filaments than the base fluid without AMA or with the incumbent AMA. The substantially longer filament lifetimes for AP-1 is associated with the presence of pronounced elastocapillary (EC) thinning behavior where the filament thinning dynamics show an exponential decay that follows $D_{mid} \sim \exp(-t/3\lambda_E)$. The coating with AP-1 has an extensional relaxation time of λ_E=275 ms which leads to a filament lifetime of longer than 2.5 s. The coating without AMA or with the incumbent AMA fluid have short lived filament lifetimes less than 0.25s and no pronounced EC thinning. These findings suggest that AMAs that impart strong non-linear extensional rheology to the coating fluid may be required to suppress mist to ultra-low levels at high coat speeds.

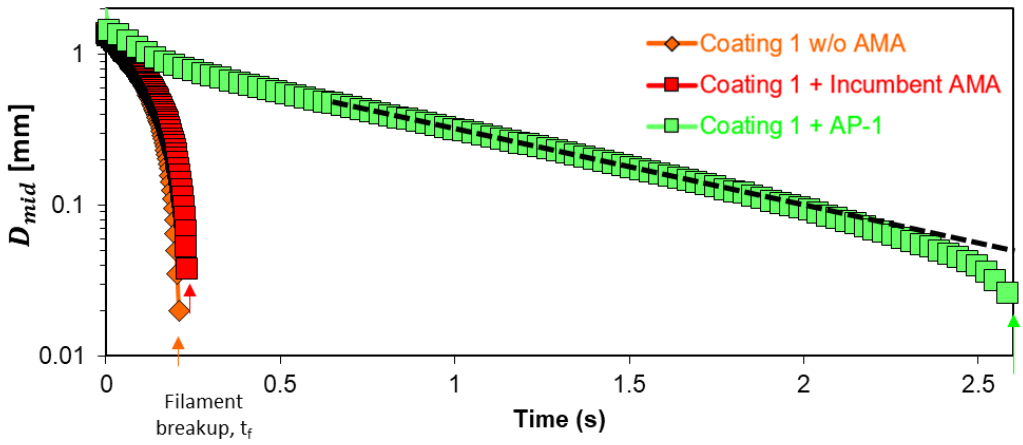


Figure 9. CaBER test result of coating fluids with and without AMA: CaBER diameter vs time after step strain.

Taking it a step further, the AP-1 was formulated into model coating **2** and tested on a real-sized industrial high-speed coater at 1,000 and 1,300 m/min, yielding similar results. As shown in Figure 10, model coating **2**, without AMA, displayed a high level of misting: 281.00 mg/m^3 at 1,000 m/min. When incumbent AMA was added, the mist level significantly decreased to 10.00 mg/m^3, which is close to the result obtained from the mist tester. However, the level was still above the acceptable threshold of 5.00 mg/m^3. In contrast, the coating with the same wt% of AP-1 showed a much reduced mist level of 2.04 mg/m^3, being lower than the threshold. To better understand the potential of the new AMA, the coatings were also tested at a higher speed of 1,300 m/min. As expected, the mist generation became heavier when the coating speed increased. The mist level of the incumbent AMA based coating increased from 10.00 to 17.80 mg/m^3. In comparison, the mist level of AP-1 based coating only slightly increased from 2.04 to 2.50 mg/m^3, yet still below the threshold. The industrial coater trial confirmed the mist test results obtained from the mist tester and validated the capability of the internal methodologies on mist performance investigation. After validating the superior mist reduction performance of the new prototype, we further optimized the prototype using the Design of Experiment (DOE) approach, resulting in the 4th generation AMA, which laid the foundation for the development of the next generation high-speed release coating.

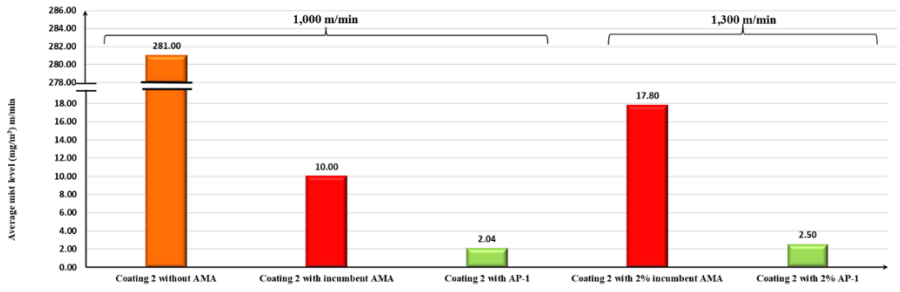


Figure 10. Mist level of coating **1** with and without incumbent and new AMA on industrial coater at 1,000 and 1,300 m/min.

3.5 Next generation high speed release coating and its performance

Considering the downstream applications, excellent mist reduction performance is just one of several key criteria that a high-speed coating must meet. A successful coating must also address other challenges from a performance perspective:

a. Good coatability is essential for ensuring smooth liner production. For the typical solventless silicone release coating, viscosity is the primary consideration.
b. Good immediate and aged cure anchorage are also crucial for silicone coatings, as this prevents issues such as blocking and silicone migration that can adversely affect downstream applications. The cure performance is typically evaluated using the extractable test, which measures the percentage of uncured silicone that can be extracted by an organic solvent. A lower extractable percentage indicates better curing and reduced amount of free migratable silicone. The industry threshold for extractable is < 5%, and lower values indicate better performance. Anchorage performance is evaluated using the rub-off resistance percentage (ROR%) test, which measures the amount of silicone remaining on the substrate after rubbing the cured coating against a specially designed felt. The industrial threshold for ROR% is > 80%, and higher values indicate better anchorage performance.
c. Total control of the release force and good release stability over time are also essential. The correct release force profile is critical for ensuring a smooth delamination process and proper use of PSA products. Additionally, the release force should remain stable and consistent over time, with minimal changes during laminate storage. Release stability is crucial for delivering predictable and reliable performance and preventing any potential production issues throughout the laminate's shelf life.

Combining the brand-new state-of-art antimist technology and Dow's cutting-edge technologies in the release coating field, the environmentally friendly solventless next-generation (next-gen) high speed coating system was successfully developed to meet the strong market need for high speed applications. The formulated step-change high speed coating was extensively tested internally *via* new mist predictive methodology, external high speed coaters, customer's high speed pilot coater, and industrial production coater to demonstrate its excellent mist reduction capability at high speeds over other commercial alternatives. For example, as shown in Figure 11, at 1,000 m/min, the next-gen high speed coating demonstrated much lower mist level (0.30 mg/m^3) than the mist level of incumbent coating **1** without AMA (175.34 mg/m^3), the incumbent coating **1** with the incumbent AMA (16.85 mg/m^3), and the competitive high speed coatings A (78.42 mg/m^3) and B (14.83 mg/m^3) respectively. Most important, the mist level of the next-gen high speed coating is also well below the targeted industrial threshold at 5.00 mg/m^3.

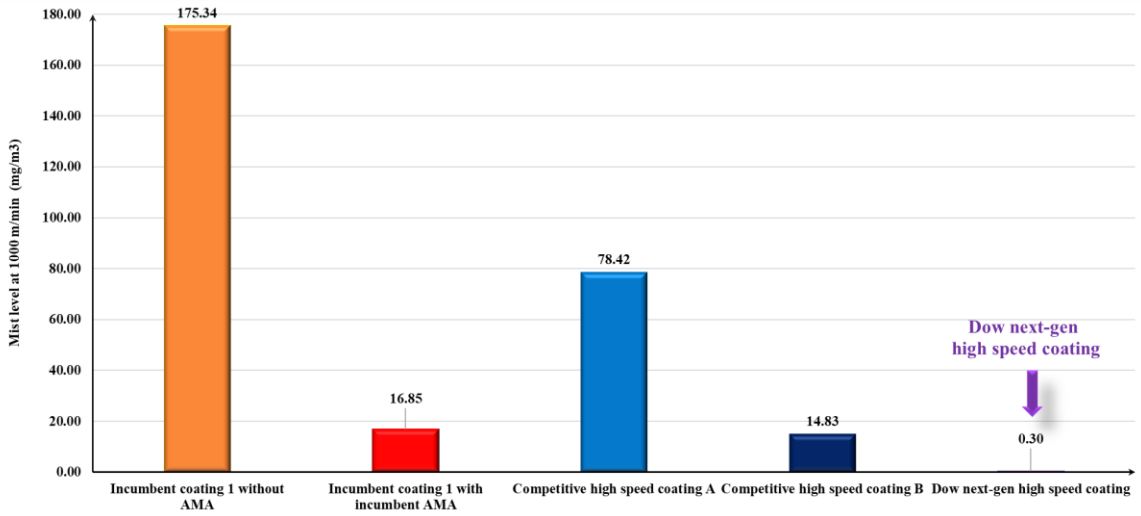


Figure 11. Mist reduction performance comparison between Dow next generation high speed coating and incumbent coatings at 1,000 m/min.

The next-gen high-speed coating has a viscosity within the typical release coating viscosity range of 100-500 cPs, ensuring that it can be easily applied. Additionally, the coating system demonstrates excellent immediate cure and immediate/aged anchorage performance, as shown in Figure 12. The next-gen high-speed coating exhibited exceptional cure performance, with an extractable percentage of much less than 5% and with immediate and aged rub-off resistance percentages of well above 80%, at high coating speed. Furthermore, the coating system displayed the correct low release force profile across delamination speeds ranging from 0.3 to 300 m/min, as shown in Figure 13. Additionally, no significant changes in release force were observed after three months of aging, indicating the coating's excellent release stability.

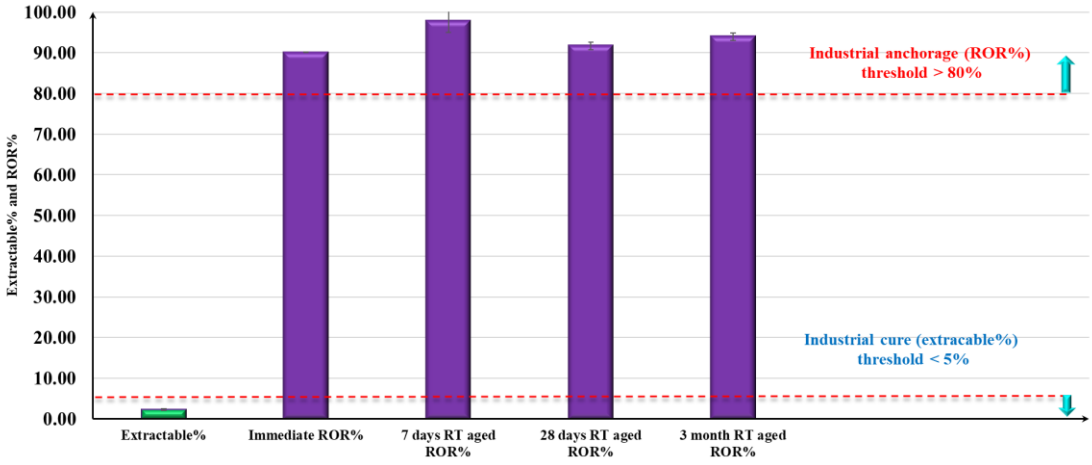


Figure 12. Cure and anchorage performance of the next-gen high speed coating.

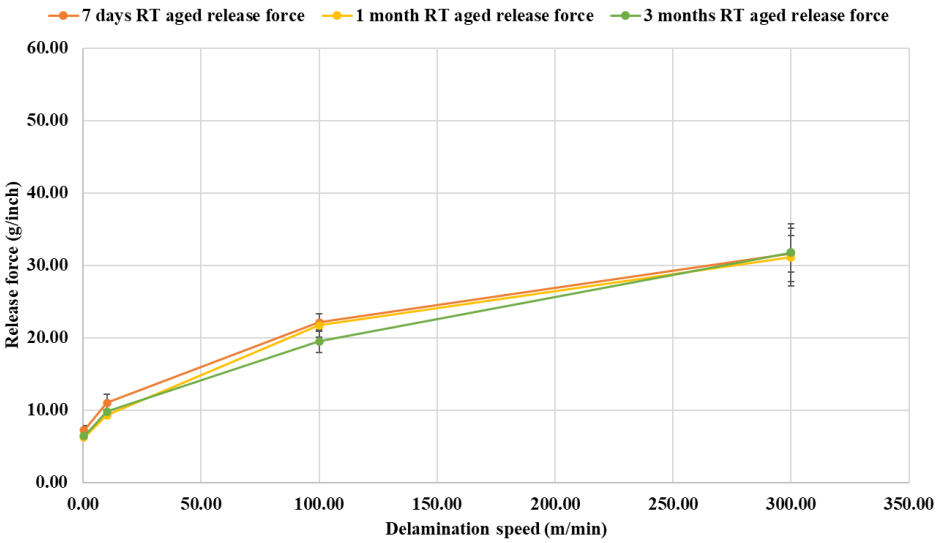


Figure 13. Release force profile of the next-gen high speed coating.

The next-gen high-speed coating system is versatile and can be combined with other state-of-the-art release coating technologies from Dow, such as advanced release modifiers, to achieve other specialized performance attributes, such as a flat release profile. The coating system's ability to meet the high-speed coating criteria while also providing exceptional curing and anchorage performance, stable release force, and compatibility with other release coating technologies makes it an ideal solution for a range of applications.

With a strong consideration for sustainability, a proprietary process was created to manufacture the new AMA and the resulting next-gen high speed coating. It was specially designed to eliminate the use of organic solvent. This innovative manufacturing route overcomes process challenges with high viscosity materials, and avoids the need for solvent stripping, which greatly reduced batch time, waste generation, and energy consumption. This approach aligns with Dow's goal of achieving a lower carbon footprint and creating a sustainable technical solution. The AMA is formulated into a solventless coating with a very low volatile organic compound (VOC) content. The innovative high speed coating is compliant with both the FDA's and EU's strict food contact regulations due to the careful design and selection of chemicals. This allows our product to be used in food applications such as direct labeling and barcoding of fruits and vegetables, which reduces plastic packaging and waste. In addition to high-speed application, the next-gen high speed coating also works well for the regular low speed coating applications, and thus it is a robust solution for all coating speeds.

4. CONCLUSIONS

Silicone release coating and liners are widely used in the pressure sensitive adhesive industry and in our daily lives. As a fast-growing market with increasing demand, the release coating industry heavily invests in high-speed production for higher production efficiency, cost reduction, and sustainability improvement. However, the increase in speed is accompanied with heavy misting, a major long-standing industrial issue. In-depth literature analysis to understand misting mechanism

enabled the development of new predictive test methodology to establish misting theories, leading to the design and development of new AMA prototypes which are capable of suppressing the heavy mist generation at high line speeds to levels well below the industrial threshold. The studies confirmed the structure/performance relationship being critical to decelerate the thinning of filaments and reduce the mist formation. The novel Dow's 4th generation antimisting technology was created based on the new findings. In combination with Dow's cutting-edge release coating expertise, the next generation high speed coating was successfully developed and commercialized for high-speed applications. The next generation high speed coating is capable of effectively reducing mist generation at high coating speed to the level well below the industrial target while, at the same time, offering efficient process-ability and superior application performance. Moreover, the strategic manufacturing route enabled a solventless process, making it a safer/more sustainable technology. Dow's next generation high speed coating enables high speed production which reduces energy consumption and carbon footprint while remaining compliant with FDA and EU food contact, undoubtedly setting a new benchmark in the release coating market.

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REFERENCES

1. Andriot, M.; DeGroot, J.; Meeks, R.; Gerlach, E.; Jungk, M.; Wolf, A.; Corning, D.; Cray, S.; Easton, T.; Mountney, A.; Leadley, S.; Chao, S.-H., Silicones in Industrial Applications. *Inorganic Polymers* **2009**.
2. Benedek, I.; Feldstein, M. M., *Technology of pressure-sensitive adhesives and products*. 2008; p 1-555.
3. Owen, M. J.; Dvornic, P. R., Surface Applications of Silicones. In *Silicone Surface Science*, Owen, M. J.; Dvornic, P. R., Eds. Springer Netherlands: Dordrecht, 2012; pp 355-374.
4. Newby, B.-m. Z.; Chaudhury, M. K.; Brown, H. R., Macroscopic Evidence of the Effect of Interfacial Slippage on Adhesion. *Science* **1995,** *269* (5229), 1407-1409.
5. Zhang Newby, B.-m.; Chaudhury, M. K., Effect of Interfacial Slippage on Viscoelastic Adhesion. *Langmuir* **1997,** *13* (6), 1805-1809.
6. AWA Global Market Study - Release Liner Annual Review. 2021.
7. Glade, K. In *Common Issues in High-Speed Silicone Coating and What to do about it*, AIMCAL Fall Technical Conference 09, Amelia Island, Florida, USA, Association of Industrial Metallizers, Coaters and Laminators: Amelia Island, Florida, USA, 2009.
8. NIOSH, OSHA PEL Project - Oil Mist. NIOSH, Ed. Centers for Disease Control and Prevention (CDC): US, 1998.
9. Greener, J.; Sullivan, T.; Turner, B.; Middleman, S., Ribbing instability of a two-roll coater: Newtonian fluids. *Chemical Engineering Communications* **1980,** *5* (1-4), 73-83.
10. Owens, M. S. Misting in forward roll coating: Structure-property-processing relationships. University of Minnesota, Minneapolis, 55455, USA, 2005.
11. Owens, M. S.; Vinjamur, M.; Scriven, L. E.; Macosko, C. W., Misting of Newtonian Liquids in Forward Roll Coating. *Industrial & Engineering Chemistry Research* **2011,** *50* (6), 3212-3219.

12. Owens, M. S.; Vinjamur, M.; Scriven, L. E.; Macosko, C. W., Misting of non-Newtonian liquids in forward roll coating. *Journal of Non-Newtonian Fluid Mechanics* **2011,** *166* (19), 1123-1128.
13. Thomson, I.; Young, F., High-speed photographic studies of ink filamentation. *Journal of the Oil & Colour Chemists' Association* **1975,** *58* (10), 389-390.
14. Ascanio, G.; Carreau, P. J.; Brito-De La Fuente, E.; Tanguy, P. A., Forward Deformable Roll Coating at High Speed with Newtonian Fluids. *Chemical Engineering Research and Design* **2004,** *82* (3), 390-397.
15. Viitaniemi, A. Silicone misting in pressure sensitive label production. Master, Tampere University, 2022.
16. Lee, C. L.; Polmanteer, K. E.; King, E. G., Flow behavior of narrow-distribution polydimethylsiloxane. *Journal of Polymer Science Part A-2: Polymer Physics* **1970,** *8* (11), 1909-1916.
17. MacPhee, J., A unified view of the film splitting process (part II). *Am. Ink Maker* **1997,** *75*, 51-56.
18. Vrij, A.; Overbeek, J. T. G., Rupture of thin liquid films due to spontaneous fluctuations in thickness. *Journal of the American Chemical Society* **1968,** *90* (12), 3074-3078.