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abstract

Pollution and the risks it poses to human health have become a global concern, and consumers are well aware of the relevant dangers. Although the negative effects of particulate matter on the respiratory system are well documented, until now their impact on the skin has not been investigated in depth. Working on the assumption that keeping particulate matter off skin is the first line of defense against pollution-induced damage, BASF has developed a novel standardized test method to assess the effects of typical cosmetic ingredients, i.e. polymers, emulsifiers, and emollients, on the adhesion and removability of pollutants. The findings have been used to create formulations that exhibit clear anti-adhesion and rinse-off (removability) effects.

Air pollution is one of the major environmental health risks facing mankind today. More than 80 percent of people who live in urban areas that monitor air pollution are exposed to levels that exceed World Health Organization (WHO) limits. When talking about air pollution, many people first think of vehicle exhaust fumes, but we encounter different types of pollutants on an everyday basis. In fact, airborne particulate matter and other pollutants come from a number of different sources, both anthropogenic and natural in origin. Some of the most important anthropogenic sources are discharge from industrial facilities, waste incineration and vehicle emissions, whether based on fossil fuels or other energy sources. Natural sources of pollutants include dust and sand storms, pollen, or ash from volcanic activity.

Multifaceted Effects of Pollutants on Human Skin

Very small particles can travel freely through the air and air and can be inhaled, which may play a role in the development of serious health effects, e.g. respiratory and cardiovascular disease. However, people are not as aware of the harmful effects that pollutants can have on the skin, and which can result in e.g. premature aging. Particulate matter can consist of ultrafine, fine and coarse particles, with aerodynamic diameters measuring < 2.5 µm, 2.5–10 µm, or 10 µm, respectively. These particle sizes are particularly relevant to respiratory diseases. Our skin, however, is exposed to particulate matter of all sizes. Negative effects are manifold in nature and can range from aesthetic changes (e.g. a dirty face due to coal dust or clogged pores) to effects on a cellular level, depending on the level of particle exposure and the mode of action. Although the impact of ambient pollution on skin has not been the focus of investigations as much as its respiratory and cardiovascular effects, the number of relevant studies has increased noticeably in recent years. *Vierkötter et al.* [1] assessed the impact of air pollution on the skin of Caucasian women aged 70–80 years. Increased exposure to particulate matter derived from soot and/or traffic correlated to an increase in facial pigment spots, also known as lentigines, age or liver spots. A further study by the same group, but focusing on volunteers of Caucasian and Asian ethnicities, also found a correlation between traffic-related air pollution and the development of lentigines [2]. *Nakamura et al.* [3] found that lentigo formation is not only a potential result of UV radiation, but can also be induced by environmental factors. They introduced the term "environment-induced lentigo" and recommended special protection in addition to UV protection. In an initial study using porcine skin, *Pan et al.* [4] assessed the impact of particulate matter on the skin barrier function. They observed increased drug absorption due to skin barrier damage. Ambient air pollution has also been reported to affect skin health and the development of acne [5].

Adhesion and Removability of Particulate Matter

Due to the multifactorial nature of pollution and its wide-ranging effects, there is no "one size fits all" approach or method to assess the effects pollutants can have on the skin, or how to counteract them. With the rationale that avoiding the adhesion of particles is one of the first lines of defense, the effects of formulation components on the adhesion and removability (i.e. rinse-off from pretreated skin) of a model pollutant was assessed. A standardized test method for evaluating the effects of polymers, emollients and emulsifiers on pollutant adhesion and removability was developed and the insights used to create new and effective formulations.

Experimental Set-up

In general, experiments were conducted on the volar forearm of 11 Caucasian volunteers who provided the volar forearm was gently cleaned with ethanol applied to a tissue. Once the skin was dry, the test product was applied and evenly distributed using a clean, soft brush. Polymers were tested in simple formulations as aqueous solutions with a pH value of 6.5 and 1 percent active matter. Emollients and emulsifiers were tested as simple formulations. The product was left to dry for 10 minutes. Initial pictures were taken (**Fig.1.1**) using a camera placed directly over the test area. The camera box was designed specifically for use on the forearm and was constructed in such a way that it created consistent lighting while blocking ambient light. The model pollutant (30 mg activated charcoal; average particle size of 80 µm [Carl Roth] or 10 mg of 2.5 µm [Cabot Corporation]) was then applied. Using activated charcoal avoided the toxicological effects associated with pollutants originating e.g. from vehicle emissions. The model pollutant was applied using a 5-second blast of air, using a closed application system to avoid particle inhalation. Further pictures were then taken (**Fig. 1.2**). A rinsing procedure was then performed in which 500 milliliters of lukewarm water was poured slowly and evenly over the test area. Following rinse-off, the area was dabbed dry with a paper towel. Pictures were taken prior to and after rinse-off (**Fig. 1.2, 1.3**). Image-based analysis was used to determine the mean lightness of the test

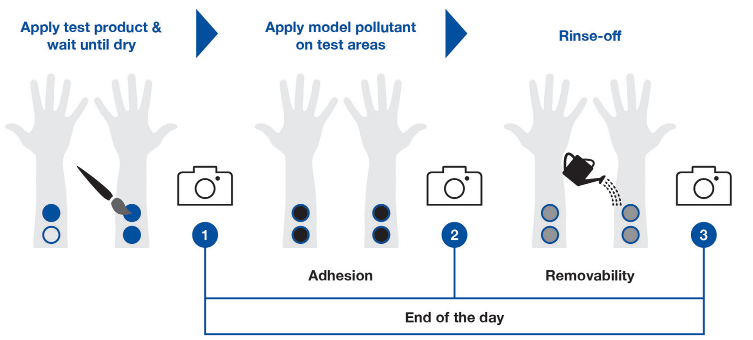

Fig. 1 Test method

Polymers	Emollients	Emulsifiers
Cosmedia® Ultragel 300 (INCI: Polyquaternium-37)	Petrolatum	Eumulgin® VL 75 (INCI: Lauryl Glucoside (and) Polyglyceryl-2 Dipolyhydroxystearate (and) Glycerin)
Rheocare® C Plus (INCI: Carbomer)	Myritol® PGDC (INCI: Propylene Glycol Dicaprylate/Dicaprate)	Emulgade® PL 68/50 (INCI: Cetearyl Glucoside (and) Cetearyl Alcohol)
Tinovis® GTC UP (INCI: Acrylates/Beheneth Methacrylate Copolymer)	Myritol® 318 (INCI: Caprylic/ Capric Triglyceride)	Eumulgin® Prisma (INCI: Disodium Cetearyl Sulfosuccinate)
Polyurethane-39	Cegesoft® PS 6 (INCI: Vegetable Oil)	Eumulgin® ES (INCI: PPG-5-Laureth-5)
Rheocare® HSP-1180 (INCI: Polyacrylamidomethyl-propane Sulfonic Acid)	Cetiol® CC (INCI: Dicaprylyl Carbonate)	Eumulgin® L (INCI: PPG-1-PEG-9 Lauryl Glycol Ether)
Luviset® Clear AT 3 (INCI : VP/Methacrylamide/Vinyl Imidazole Copolymer)	Cetiol® J 600 (INCI: Oleyl Erucate)	Eumulgin® CO 40 (INCI: PEG-40 Hydrogenated Castor Oil)
Luvimer® 100P (INCI: Acrylates Copolymer)	Cetiol® Ultimate (INCI: Undecane (and) Tridecane)	Lanette® E (INCI: Sodium Cetearyl Sulfate)
Luviquat® Supreme AT 1 (INCI: Polyquaternium-68)	Eutanol® G (INCI: Octyldodecanol)	Cutina® GMS SE (INCI: Glyceryl Stearate SE)
Luviskol® Plus (INCI: Polyvinylcaprolactam)	Cetiol® LC (INCI: Coco-Caprylate/Caprate)	Eumulgin® SG (INCI: Sodium Stearoyl Glutamate)
Cosmedia® DC (INCI: Hydrogenated Dimer Dilinoleyl/Dimethyl-carbonate Copolymer)		Plantapon® LGC Sorb (INCI: Sodium Lauryl Glucose Carboxylate (and) Lauryl Glucoside)
Luvigel® EM (INCI: Caprylic/Capric Triglyceride (and) Sodium Acrylates Copolymer)		Emulgade® Sucro Plus (INCI: Sucrose Polystearate (and) Cetyl Palmitate)
Cosmedia® SP (INCI: Sodium Polyacrylate)		Eumulgin® B2 (INCI: Ceteareth-20)
Hispagel® 200 (INCI: Glycerin (and) Glyceryl Polyacrylate)		
Luviset® One (INCI: Acrylates/ Methacrylamide Copolymer)		
Luviflex® Soft (INCI: Acrylates Copolymer)		

Tab. 1 Typical formulation components: polymers, emollients and emulsifiers tested

area and the amount of model pollutant adhering to the skin. This was then used to assess pollutant adhesion and rinse-off performance. The Grubbs' test for outliers was used to detect and eliminate data that was not within normal range. The Tukey's honest significance test was performed to check if the results were significantly different from one another with a confidence level of at least 95 percent.

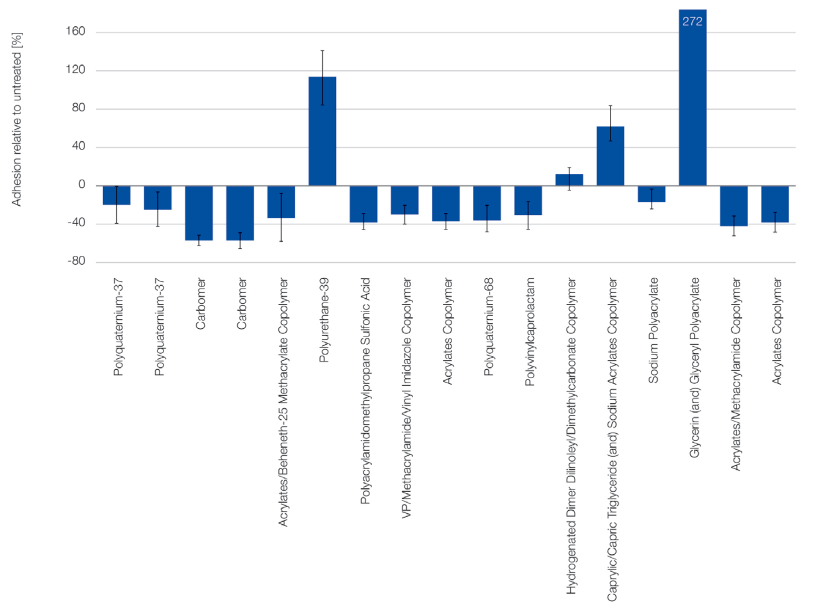

Fig. 2 Anti-adhesion test using aqueous polymer solutions (1 percent): amount adhering to the skin in relation to untreated skin (baseline = 0); the higher the score, the more PM adheres to the skin

Proof of Concept

When evaluating **polymers**, most led to a reduction in adhesion compared to the untreated, polluted skin. Rheocare® C Plus (INCI: Carbomer) achieved the best result with a reduction of nearly 60 percent. Four out of 15 polymers tested increased the adhesion of particulate matter: Polyurethane-39, Cosmedia® DC (INCI: Hydrogenated Dimer Dilinoleyl/Dimethylcarbonate Copolymer), Luvigel® EM (INCI: Capylic/Capric Triglyceride (and) Sodium Acrylates Copolymer) and Hispagel® 200 (INCI: Glycerin (and) Glyceryl Polyacrylate), with the latter boosting adhesion by as much as 272 percent compared to untreated, polluted skin (see **Fig. 2**). The removability of particles also varied. While Tinovis® GTC UP (INCI: Acrylates/Beheneth-25 Methacrylate Copolymer) reduced adhesion slightly less than Rheocare® C Plus, it exhibited better removability of the particles (also see **Fig. 3**, **3B**; not all data shown). And although Hispagel® 200 significantly increased adhesion, the removability of particles with this polymer proved to be good (see **Fig. 3, 1B**). The results of duplicate runs of the same substance proved the reliability of the developed test method (see **Fig. 2**).

Similar studies were conducted using emollients and emulsifiers. These were tested in standardized formulations, with the base remaining the same and either the emulsifier or the emollient being exchanged. Of nine **emollients** tested, Cetiol® Ultimate (INCI: Undecane/Tridecane) exhibited the least adhesion, with values similar to untreated skin. All other emollients increased adhesion. A total of 12 **emulsifiers** were tested, with the sugar-based emulsifiers Emulgade® Sucro Plus (INCI: Sucrose Polystearate (and) Cetyl Palmitate) and Emulgade® PL 68/50 (INCI: Cetearyl Glucoside (and) Cetearyl Alcohol) performing the best. There were no differences between the anionic and nonionic emulsifiers. Removability generally ranged between 40 and 60 percent, with Emulgade® PL 68/50 (INCI: Cetearyl Glucoside (and) Cetearyl Alcohol) performing best, achieving 71 percent.

The Right Set of Ingredients to Develop Effective Anti-Pollution Formulations

Typical formulations for skin care applications contain a combination of polymers, emollients and emulsifiers, along with optional ingredients such as bio-actives or UV filters. The components that exhibited the best anti-pollution performance in the first test series were used to develop skin care formulations with improved anti-pollution effects. Formulation SC-DE-17-017-48 with the best test performance contained the emollient Cetiol® Ultimate (INCI: Undecane/Tridecane), the emulsifier Emulgade® PL 68/50 (INCI: Cetearyl Glucoside

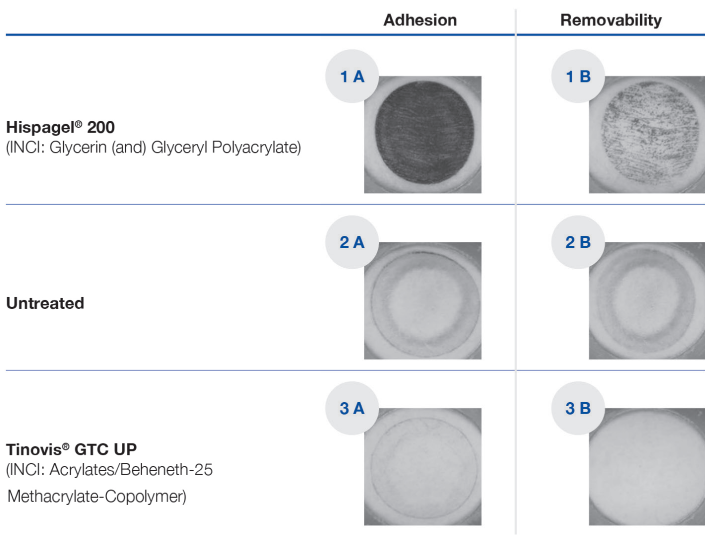

Fig. 3 Examples of adhesion (A) and removability results (B) for polymer solutions (1 percent active substance)

(und) Cetearyl Alcohol) as well as the polymers Rheocare® C Plus (INCI: Carbomer) and Tinovis® GTC UP (INCI: Acrylates/Beheneth-25 Methacrylate Copolymer). It also contained the active PatchH$_2$O®, which delivers moisturizing effects but, in contrast to Glycerin, does not increase adhesion. Experimental studies also indicate that it may be beneficial for the balance of the skin's microflora.

A further formulation was developed, SC-DE-17-017-54, containing the most efficacious ingredients and a combination of UV filters that produced a calculated and achieved sun protection factor of 10. Both formulations contained the antioxidant Tocopherol as well as the chelating agent Tetrasodium EDTA, each of which address further aspects of anti-pollution claims, e.g. reduction in oxidative stress.

Formulation SC-DE-17-017-48

Phase	Ingredients	INCI	% by weight	Function
A	Water, demin.	Aqua	85.61	
	Rheocare® C Plus	Carbomer	0.66	Rheology modifier
	Tinovis® GTC UP	Acrylates/Beheneth-25 Methacrylate Copolymer	1.00	Rheology modifier
	Edeta® B Powder	Tetrasodium EDTA	0.20	Complexing agent
B	Potassium Hydroxide (20% solution)	Potassium Hydroxide	1.83	pH Adjustment
C	Emulgade® PL 68/50	Cetearyl Glucoside, Cetearyl Alcohol	1.00	Emulsifier (O/W)
D	Cetiol® Ultimate	Undecane, Tridecane	2.50	Emollient
E	Euxyl PE 9010 (Schülke)	Phenoxyethanol, Ethylhexylglycerin	1.10	Preservative
	Sensiva SC 50 (Schülke)	Ethylhexylglycerin	0.40	Auxiliary
F	Covi-ox® T 90 EU C	Tocopherol	0.50	Active ingredient
	PatcH$_2$O®	Aqua, Glycerin, Glyceryl Polyacrylate, Trehalose, Urea, Serine, Pentylene Glycol, Algin, Caprylyl Glycol, Sodium Hyaluronate, Pullulan, Disodium Phosphate, Potassium Phosphate	5.00	Active ingredient
	Perfume "Always the Sun" (Symrise)	Parfum	0.20	Fragrance

Formulation 1

Formulation SC-DE-17-017-54

Phase	Ingredients	INCI	% by weight	Function
A	Water, demin.	Aqua	82.11	
	Rheocare® C Plus	Carbomer	0.66	Rheology modifier
	Tinovis® GTC UP	Acrylates/Beheneth-25 Methacrylate Copolymer	1.00	Rheology modifier
	Edeta® B Powder	Tetrasodium EDTA	0.20	Complexing agent
B	Potassium Hydroxide (20% solution)	Potassium Hydroxide	1.83	pH Adjustment
C	Emulgade® PL 68/50	Cetearyl Glucoside, Cetearyl Alcohol	1.00	Emulsifier (O/W)
D	Uvinul® A Plus B	Ethylhexyl Methoxycinnamate, Diethylamino Hydroxybenzoyl Hexyl Benzoate	4.00	Broad spectrum UV filter
E	Euxyl PE 9010 (Schülke)	Phenoxyethanol, Ethylhexylglycerin	1.10	Preservative
	Sensiva SC 50 (Schülke)	Ethylhexylglycerin	0.40	Auxiliary
F	Covi-ox® T 90 EU C	Tocopherol	0.50	Active ingredient
	PatcH$_2$O® A00297	Aqua, Glycerin, Glyceryl Polyacrylate, Trehalose, Urea, Serine, Pentylene Glycol, Algin, Caprylyl Glycol, Sodium Hyaluronate, Pullulan, Disodium Phosphate, Potassium Phosphate	5.00	Active ingredient
	Perfume "Always the Sun" (Symrise)	Parfum	0.20	Fragrance
G	Tinosorb® M	Methylene Bis-Benzotriazolyl Tetramethylbutyl-phenol (nano), Aqua, Decyl Glucoside, Propylene Glycol, Xanthan Gum	2.00	Broad spectrum UV filter

Formulation 2

The test formulations were then compared to two benchmark products that are marketed with anti-pollution claims and using the same experimental set-up as before. In this series, the effects of the larger and smaller particles were assessed. Although the values obtained were not the same, there were similar trends. A correlation coefficient value of R2= 0.99 was calculated, indicating a very good correlation of results. Formulation SC-DE-17-017-48 was able to reduce particle adhesion to levels below those of untreated skin. Furthermore, formulation SC-DE-17-017-54 exhibited significantly better anti-adhesion results than the benchmark products. Both formulations exhibited excellent rinse-off properties, with virtually no particles detectable on the skin at the end of the day. The benchmark products, by contrast, increased adhesion and reduced removability compared to untreated skin (**Fig. 4B**).
Because skin care products also need to address other aspects of skin care, e.g. mildness and/or skin hydration, further tests were conducted with formulation SC-DE-17-017-48. This formulation exhibited an 8-hour moisturizing efficacy, good skin tolerance, and improved sensorial attributes and acceptance compared to a market benchmark (data not shown). The results of these studies indicate that, by creating tailor-made formulations, effective anti-pollution products can be developed without forfeiting other important aspects of skin care, such as moisturization or sensation on the skin.

Conclusion

Consumer awareness of the adverse effects of pollution is on the rise, and there is an increasing number of reports indicating that pollutants can lead to skin damage. A study was initiated to systematically assess the effects that formulation components can have, targeting a decrease in particle adhesion and improvement in particle removal as a means to help mitigate the adverse effects of particulate pollutants. A novel standardized test method was developed where activated charcoal was applied to volunteers' skin. The systematic approach revealed clear differences in particle adhesion and removability depending on the substances applied. The findings were then used to develop formulations that had clear anti-adhesion and removability effects, while addressing other important aspects of skin care products such as skin compatibility, moisturization, or sensation on the skin. With this approach, specific properties of both individual components and emulsion systems can be identified. The insights from the studies were then used to successfully create effective formulations that help safeguard the skin against particulate matter.

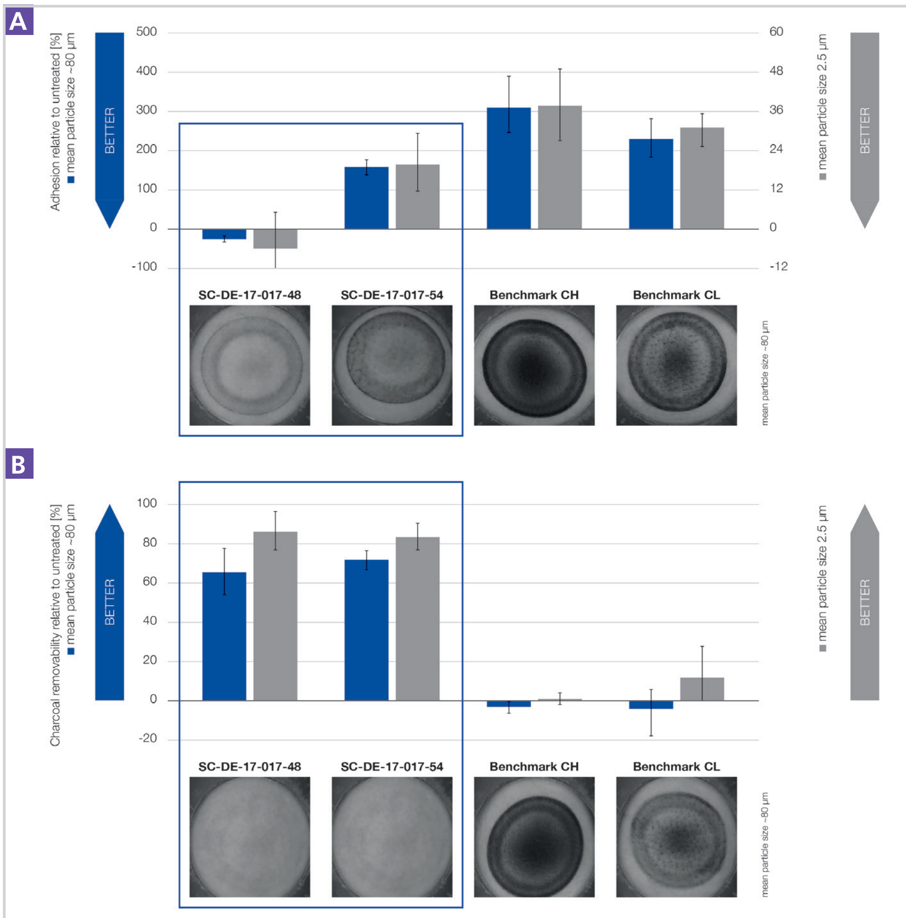

Fig. 4 Adhesion (4A) and removability performance (4B) of the formulations compared to benchmark products, relative to the untreated skin (baseline = 0); charcoal average diameters of 80 µm (blue) and 2.5 µm (grey)

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