

Accelerated wear testing of CitroXProtect

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CONFIDENTIAL

Abstract

Citrox Protect from Citrox Biosciences Ltd was applied to glass substrates according to the manufacturer's instructions and subjected to wear simulating 500, and multiples thereof, human finger touches. Contact angle measurements were undertaken to monitor the presence of the coating. The coating maintained its hydrophobic integrity even after 5000 touches, the maximum number investigated.

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1 Background

Citrox Bioscience Ltd. requested an independent study into the abrasion resistance of the product and an overview of its capability to continue acting as a hydrophobic barrier over a prolonged period during typical wear and tear associated with hard surface touch points.

The study was commissioned with Jeremy J. Ramsden, a leading authority on nano technologies. Jeremy has an academic background that spans mathematics, physics, chemistry, cell biology, biochemistry and more recently integrated nano science and nano technology.

2 Materials

A bottle containing 500 mL of CitroxProtect was provided by Dirk Kreisler, Nano4You GmbH (batch number 2007165-CP). Substrates were 75 × 24 × 2 mm glass microscope slides. They were cleaned by brushing in warm water and detergent ("Essential Waitrose washing up liquid original", containing 15–30% anionic surfactants, 5–15% amphoteric surfactants and < 5% non-ionic surfactants), followed by thorough rinsing in deionized water and then allowed to drain and dry in air. When completely dry, CitroxProtect was applied to a soft cotton cloth and the surface was polished with a circular motion. The coated substrates were then left undisturbed for 72 hours. The presence of the coating could not be discerned by visual inspection. During coating and storage the temperature was 23.0 ± 1.5 °C and the relative humidity was $53 \pm 3\%$.

3 Wear testing

A human finger was simulated from a strip of soft leather 22 mm wide formed into a cylinder, external diameter 20 mm. The artificial finger was mounted using a customized workplace on the head of a general-purpose robot and pressed down at a speed of 20 mm/s until a force of 310 g (3 N) was achieved, and then immediately withdrawn, corresponding to a typical moderate finger press. This operation was repeated 500 times in each of three places with 2 mm lateral displacement between them, such that after deformation of the leather cylinder during pressing, an area of 8×22 mm was uniformly touched.

Touching was carried out at a temperature of 25.0 ± 0.5 °C and $51 \pm 3\%$ relative humidity.

4 Contact angle measurement

Contact angle measurement is a highly sensitive method for determining alterations in surface properties, including the presence of films too thin to detect by other means. It is, therefore, particularly suitable for investigating Citrox Protect coatings and their possible removal by wear. It is noted that (according to the label) the product “repels aqueous and greasy liquids . . . Coated surfaces become water repelling . . .”. From appropriate contact angle measurements, liquid repellence, especially hydrophobicity, can be readily quantified. A simple method for doing this is simply to measure the contact angle of water. According to Vogler, a surface is hydrophobic if its contact angle exceeds 65° [4].

This is, however, rather arbitrary and a much more rigorous assessment is to determine the three cardinal surface tension components, $\gamma^{(LW)}$, γ^{\oplus} and γ^{\ominus} , where: the superscript LW denotes the Lifshitz–van der Waals component (comprising the London–van der Waals, Debye and Keesom interactions), always attractive; the super-script \ominus denotes the electron-donating component (Lewis base or hydrogen bond acceptor), also known as *dativit'a* [1]; and the superscript \oplus denotes the electron-accepting component (Lewis acid or hydrogen bond donor), also known as *recettivit'a*. The electron donor–acceptor interactions are collectively denoted *da* and can be either attractive or repulsive [2, 1]. These three components fully characterize the surface energy of a coating. They can be determined from three simultaneous measurements of the contact angles of three liquids differing in the values of these components [2, 1]. Good practical choices of these liquids are those given in Table 1. Diiodomethane is completely apolar and represents grease, and Formamide has properties somewhat intermediate between those of the other two, and represents a great class of polar solvents such as Ethanol, Propanol and Acetone.

Table 1: Properties of some liquids useful for surface tension measurements. Surface tension units are mN m^{-1} .

Liquid	$\gamma^{(LW)}$	γ^{\oplus}	γ^{\ominus}	B.P./°C	Viscosity/cP
Diiodomethane	51	0.0	0.0	182	2.6
Formamide	39	2.3	40	210	3.3
Water	22	25.5	25.5	100	1.0

After the conclusion of the touching operation, 10 μL droplets of Diiodomethane (99%), Formamide ($\geq 99.5\%$) and Water (triply distilled) were applied to the touched area of the coated substrates. Contact angles were measured with a laboratory-built device at a temperature of 23.0 ± 1.5 °C, $57 \pm 6\%$ relative humidity, and an atmospheric pressure of 0.9955 ± 0.0005 bar.

The relationship between contact angle θ and surface tension is given by Young's law:

$$\gamma_2 \cos \theta = \gamma_1 - \gamma_{12} \quad (1)$$

(written with the assumption that the surface tension of solid or liquid in contact with their respective vapours is equal to the single-substance surface tension), where subscripts 1 and 2 denote, respectively, the solid (possibly coated) substrate and the liquid (typically selected from Table 1). This equation was extended by Dupré to explicitly include the different energetic components of the surface tension:

$$[\gamma_2^{(\text{LW})}/2 + (\gamma_2^{\oplus}\gamma_2^{\ominus})^{1/2}](1 + \cos \theta) = (\gamma_1^{(\text{LW})}\gamma_2^{(\text{LW})})^{1/2} + (\gamma_1^{\oplus}\gamma_2^{\ominus})^{1/2} + (\gamma_1^{\ominus}\gamma_2^{\oplus})^{1/2} . \quad (2)$$

Once the experimental contact angle measurements are available, this data and the parameters given in Table 1 (the γ s with subscript 2) give us three simultaneous young–Dupré equations (2) which are solved to yield the three unknowns $\gamma_1^{(\text{LW})}$, γ_1^{\oplus} and γ_1^{\ominus} ; i.e., the three surface tension components of the coating.

Hydrophobicity is related to the coating–water interfacial energy ΔG_{1w} , sub-script w denoting liquid water. The most convenient way of assessing hydrophobicity is to determine the sign of ΔG_{1w1} ; i.e., the energy of interaction between two identically coated surfaces in the presence of water. If it is positive the coating is hydrophobic and if it is negative the coating is hydrophilic [3]. ΔG_{1w1} is directly related to the surface tension of the 1–2 interface:

$$\Delta G_{1w1} = -2\gamma_{12} \quad (3)$$

and the LW and da components are combined linearly:

$$\gamma_{12} = \gamma_{12}^{(LW)} + \gamma_{12}^{(da)} . \quad (4)$$

The surface tension combining laws are [2, 1]:

$$\gamma_{12}^{(LW)} = \left(\sqrt{\gamma_1^{(LW)}} - \sqrt{\gamma_2^{(LW)}} \right)^2 \quad (5)$$

and

$$\gamma_{12}^{(da)} = 2 \left(\sqrt{\gamma_1^{\oplus}} - \sqrt{\gamma_2^{\oplus}} \right) \left(\sqrt{\gamma_1^{\ominus}} - \sqrt{\gamma_2^{\ominus}} \right) . \quad (6)$$

5 Results

Table 2: Mean contact angles (in degrees). Uncertainties are ± 3 .

	No touches	Diiodomethane	Formamide	Water
Uncoated		24	25	28
0		56	68	81
500		51	76	81
1000		47	67	82
2000		35	68	76
5000		48	60	78

6 Discussion

Clearly the coating imparts hydrophobicity to the surface according to Vogler's criterion (water contact angle greater than 65°), and it is not significantly de-graded even after 5000 touches. This conclusion can be refined by computing the surface tension components.

6.1 Surface tensions

Using the data from Table 2 and equations (2), surface tensions were calculated (Table 3).

Table 3: Mean surface tensions. Uncertainties are $\pm 12\%$.

No touches	$\gamma^{(LW)}/\text{mN m}^{-1}$	$\gamma^{\oplus}/\text{mN m}^{-1}$	$\gamma^{\ominus}/\text{mN m}^{-1}$
Uncoated	46.5	0.15	47.5
0	30.9	0.01	9.6
500	33.7	0.93	15.4
1000	35.9	0.04	8.3
2000	42.0	1.07	15.9
5000	35.4	0.11	8.2

6.2 Hydrophobicity

From the data in Table 3, the coating–water interfacial energy ΔG_{1w1} can be calculated according to equations (3) to (6). The results are plotted in Figure 1.

From the surface tension component data, it can also be concluded that the coating maintains its grease-resistant, as well as hydrophobic, properties.

6.3 Contributions to uncertainty

The dominant contribution to uncertainty would appear to be the skill of the coater. It is, however, a skill that should be readily perfected with practice.

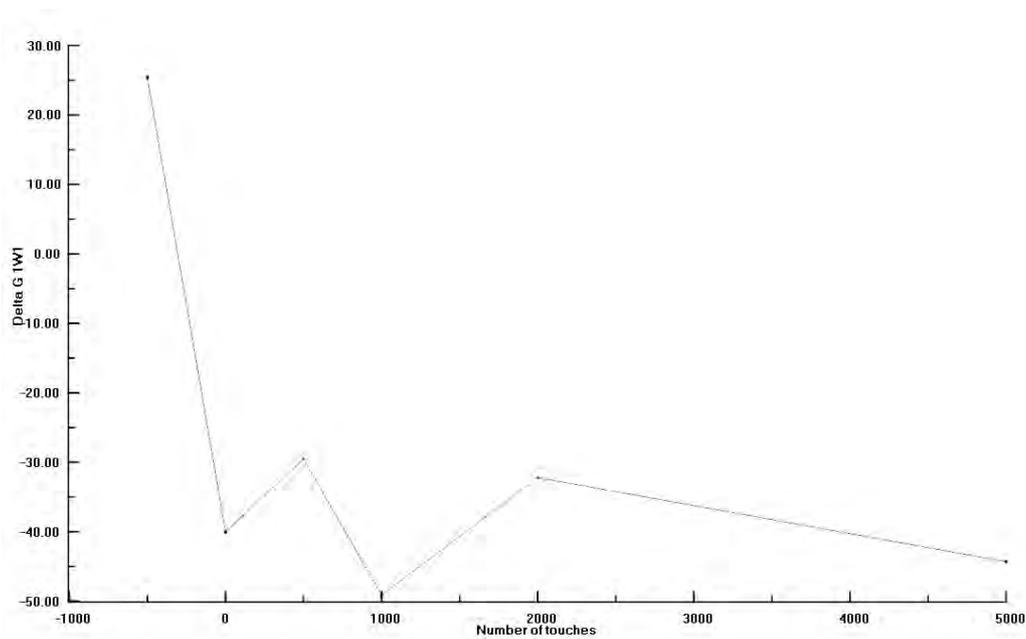


Figure 1: Plot of $\Delta G_{1w1}/\text{mJ m}^{-2}$ of Citrox Protect-coated glass v. the number of simulated finger touches. The uncoated glass is represented by -500 touches. The overall uncertainty in the individual values is estimated at about $\pm 10 \text{ mJ/m}^2$, hence there is probably no significant change in the parameter for up to 5000 touches.

The difficulty is that no immediate feedback (especially visual) on the quality of the coating is available. Nevertheless, the margin of tolerable imperfection may be quite high; it seems unlikely to contribute to poor wear resistance.

Many uncontrolled variables could potentially affect the results, including the duration of curing after coating and prior to using. However, the manufacturer indicates that 24 hours is adequate, hence in the present investigation there was a good margin of safety.

If the actual uncertainties are actually smaller than the conservative estimate indicated on Figure 1, a possible explanation for the apparent improvement in properties with touching could be due to the action of repeated touching imposing post-polymerization polishing on the coating. Much more extensive testing would be needed to firmly establish the existence of such a phenomenon.

7 Conclusions

Citrox Protect, when properly applied, is able to resist finger touches corresponding to 6 months' usage (depending on the environment), as evinced by contact angle measurements using water, an apolar liquid, and a liquid of intermediate polarity. The coating clearly maintains its hydrophobic and grease-repellent properties.

References

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