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Investigations into the reduction of powder adhesion to stainless steel surfaces by surface modification to aid capsule filling

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Abstract

The adhesion force of powder particles to stainless steel surfaces, which had been modified by various metal coatings, has been measured using a centrifuge technique. The surfaces were characterised by surface roughness and surface free energy measurements, whereas the particles, which had a particle size of 32–45 μm, were characterised by their surface free energy only. The roughness of the surfaces was found to be similar, so that changes in the adhesion properties of the powders to these surfaces could not be due to a change in this surface property. However, there was a major difference in the surface free energy parameters of the surfaces. The surface free energy varied from a nearly non-polar character to a strong Lewis-base. The adhesion force of pregelatinised starch and lactose monohydrate particles increased with the increasing base character of the surfaces. In principle this behaviour could also be seen for calcium carbonate particles. However, here the order of the adhesion forces to the surfaces tested was disrupted on one occasion because of a pronounced influence of particle and surface hardness on this property. In general, the ranking of the adhesion forces matched observations made during capsule filling on a Bosch GKF-400 tamp-filling machine. It was therefore concluded that a metal coating of the tamping pins would be able to reduce powder adhesion. In order to identify the best coating, centrifugal adhesion force measurements could be undertaken, or surface free energy measurements could be made. The results found suggest that a surface finish by means of chromium nitride coating provided, in most cases, a significant reduction of the powder adhesion. For very hard powder particles such as inorganic excipients the hardness of the surfaces must also be increased. In these cases plasma-coating of chromium appears helpful. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Capsule filling; Powder adhesion; Surface free energy; Surface roughness; Tamp-filling machine

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1. Introduction

The manufacture of powder filled hard gelatine capsules involves two basic requirements: firstly, the filling process must run over many hours on an industrial scale machine without interruptions, and secondly, the incorporated drug must be released in an appropriate time after administration of the capsule (Jones, 1988). In order to satisfy the two requirements simultaneously, formulation parameters and machine settings should be optimised. To date most authors have concentrated on the optimisation of the flow and packing properties as one main feature of the formulation. However, on an industrial scale large lubricant and glidant concentrations are employed (Jones, 1995), which seem not to match optimal concentrations in terms of powder flow (Podczeck and Miah, 1996). High concentrations of lubricant are also prone to hinder drug dissolution and should therefore be avoided (Newton, 1987). One reason for the larger lubricant concentrations might be the adhesion of particles to the dosator nozzles or tamping pins. Even for powders with satisfactory flow properties such as microcrystalline cellulose powder coating of the dosator nozzle walls has been observed (Patel and Podczeck, 1996).

One possible way to avoid excessive lubricant concentrations could be a surface modification of those parts of a capsule filling machine, which are in permanent contact with the powder and also in motion, because here the build-up of powder adhesion layers is particularly critical. In a tamp-filling machine powder adhesion is critical at the dosing disc, the tamping ring and the tamping pins. (In the Bosch tamp-filling machines, the ‘support plate’ of the former H&K machine has been replaced by a ‘tamping ring’. While this constructional change has some technical advantages, the function of the tamping ring of the Bosch machine and the support plate of the H&K machine are identical.) Stickiness between the dosing disc and tamping ring can be problematic. Hence, the gap between the dosing disc and the tamping ring can be adjusted to minimise the sticking of the powder between them. However, the tamping pins are fully exposed to the adhesion properties of the formulation and therefore require special attention.

The aim of this work was to test the influence of metallic coatings on the adhesion properties of powders to tamping pins.

2. Materials and methods

The following excipients have been used: lactose monohydrate (Borculo Whey Products, Saltney, UK; batch 033505), pregelatinised starch (Starch 1500®, Colorcon, Dartford, UK; batch 012003) and heavy precipitated calcium carbonate (Merck, Poole, UK; batch 618535).

The powders were fractionated with an air jet sieve (Alpine, Augsburg, Germany) to obtain a particle size fraction of $-45+32$ μm. The powder fractions desired were stored over silica gel in closed glass bottles. Unfractionated powder was also used and for this purpose stored at ambient room conditions in the packaging as received.

The mass of the particles was determined using an autobalance (AD-4, Perkin-Elmer, Connecticut, USA). An accurately weighed sample was suspended in methylendiiodide (Aldrich, Fillingham, UK), and the particles were counted with an image analyser (Solitair 512, Seescan, Cambridge, UK) connected to an Olympus microscope (BH-2, Olympus, Tokyo, Japan) via a CCD-4 black/white camera (Rengo, Toyohashi, Japan). The results are the mean and S. D. of five replicates: 69 ± 4, 58 ± 5, and 84 ± 3 ng for lactose monohydrate, pregelatinised starch and calcium carbonate, respectively.

Test surfaces of 12.5 mm diameter and 3 mm thickness were provided by Bosch (Waiblingen, Germany). They were made from stainless steel. Some were coated with chromium nitride, carbon, chromium carbide or plasma-chromium. The tamping-pins with similar coatings were provided for a Bosch GKF-400 tamp-filling machine.

The surface roughness of the test surfaces was assessed using a non-contact laser profilometer (UBM Microfocus Measuring System, UBM Meßtechnik, Ettlingen, Germany). The light spot diameter of the sensor is 1 μm and the sensor aperture angle is 53°. Measurements were performed in 3D-mode at a frequency of 100 points/s and a measuring depth of ± 50 μm. Under these conditions, the measuring error in the vertical direction is ± 0.006 μm. On each surface a 3 × 3 mm area was measured. The measuring point density was 250 points/mm in the x- and y-direction. Three discs per test surface were evaluated. Classical surface roughness parameters (R_a, arithmetic mean of the departures of the roughness profile from the mean line; R_q, root mean square deviation of the asperity height distribution; R_{tm}, average peak-to-valley ratio), a fractal dimension (FD), and the correlation distance (β, autocorrelation analysis) were selected as characteristic surface roughness parameters in this study.

Measurements to determine the surface free energy of the test surfaces were undertaken by means of the sessile drop technique. Prior to analysis, the surfaces were cleaned with ethanol in an ultrasonic bath for 3 min. Further attempts to remove possible oxidation products were not made to match the practical use of these surfaces. The surfaces were positioned in front of an image camera (CCD-4 miniature video camera, Rengo, Toyohashi, Japan) which was equipped with a zoom lens (18–108/2.5, Olympus, Hamburg, Germany) and connected to an image analyser (Sonata, Seescan, Cambridge, UK). The contact angle against liquids was measured. A micro-syringe was used to deposit a droplet of 3 mm diameter on top of the surface, the image was taken and the contact angle determined from the width of the drop at the solid surface (a) and the height (h) of the drop ($\tan \theta/2 = 2h/a$). For contact angles larger than 90° the height of the drop between the solid surface and the equator of the drop (c) was used ($\tan(180 - \theta) = a/2c$). Three liquids of different polarity were used: distilled water, ethylene glycol (Sigma, St. Louis, USA) and α-bromnaphthalene (Acros Organics, Geel, Belgium). Ten replicate values for the contact angle for each liquid on each surface were determined, and the surface free energy values were then calculated from the mean values of the contact angles. Hence, all surface free energy values listed in the text appear as single values without S.D.

Experiments to obtain the surface free energy of the powders were also undertaken with the sessile drop technique. Flat plates of 20 × 20 × 3 mm were produced using a Specac 15000 hydraulic press (Specac, Kent, UK) and 220 MPa compaction pressure. A dwell time of 1 min was used. Further assessment followed the procedure described for the test surfaces. However, glycerol (Acros Organics, Geel, Belgium) was used instead of water to avoid dissolution and full wetting.

The adhesion force between the powder particles and the test surfaces was determined using a centrifuge technique (Podczeck and Newton, 1995). An ultracentrifuge (Centrikon T-1080, Kontron Instruments, Milan, Italy) with a vertical rotor (TV-850, DuPont Sorvall, Wilmington, USA) and a set of specially developed adapters (Ventura Scientific, Orpington, UK) was used. The test surfaces were dusted with powder. It was confirmed microscopically that only single particles had deposited on the surface. The test surfaces were placed into the adapters so that the dusted surfaces faced the centre of the rotor. A defined press-on force was applied to simulate a tamping force acting on the particles and pin surfaces during automatic capsule filling: 2.82×10^{-5}, 2.80×10^{-5} and 2.86×10^{-5} N for lactose monohydrate, pregelatinised starch and calcium carbonate, respectively. Assuming a true area of contact of 2.5% (Podczeck et al., 1996a) these press-on forces are equivalent to a tamping force of 30 N, which is the commonly achieved force in a Bosch GKF machine (see the user's manual, Robert Bosch, Waiblingen, Germany). Afterwards the number of particles initially adhering to the test surfaces was determined using the image analyser described for the assessment of the mass of the particles. The surfaces were illuminated using a cold light source (High Light 3002, Olympus Europe, Hamburg, Germany), which was attached parallel to the surface ca. 1.5 cm from the periphery. The two light beams were placed at an angle of 180° to each other to minimise the formation of shadows. The initial number of particles was about 500 per surface, and six surfaces were used in parallel in each experiment. A spin-off force was applied and the number of particles that remained adhered was determined. An adhesion force distribution was obtained by successively increasing the spin-off force after each counting. The adhesion force distributions fol-

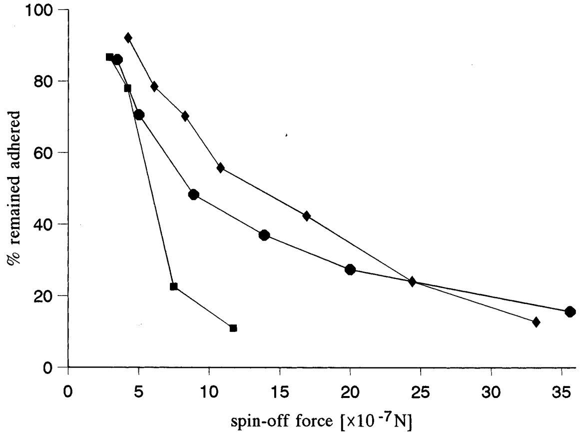

Fig. 1. Adhesion force distributions of powders to stainless steel test surfaces (arithmetic mean of six replicates). ■, Pregelatinised starch; ●, lactose monohydrate; ◆, calcium carbonate.

lowed a logarithmic normal distribution function. They were therefore characterised with the geometric mean diameter and the geometric S.D. of the adhesion force using SPSS 7.5 (SPSS, Woking, UK).

Powder filling into hard gelatine capsules size 1 (Capsugel, Colmare, France) was undertaken on a Bosch GKF-400 tamp-filling machine (Robert Bosch, Waiblingen, Germany). The powders were filled first without addition of lubricant. For lactose monohydrate and calcium carbonate filling was repeated after addition of 1% magnesium stearate (BDH, Poole, UK). All filling tests were limited to a maximum of 0.5 h. Only three pins for each coating could be obtained. Hence, these were used to replace the stainless steel pins at tamping station 5, i.e. at the point of maximum tamping pressure.

3. Results and discussion

A typical example of a set of adhesion force distributions is provided in Fig. 1. The mean geometric adhesion forces and geometric standard deviations of all experiments are listed in Table 1. The adhesion of all three powders to the untreated stainless steel surfaces was the greatest. Using pregelatinised starch, the use of coated surfaces reduced the adhesion force only slightly, although the differences obtained are statistically significant (ANOVA: $F = 36.16$, $p < 0.001$). During capsule filling it was also found that pregelatinised starch could be filled without addition of a lubricant over the whole filling time. There was no

Table 1
Mean geometric adhesion forces (F_{ad}) and geometric S.D. (σ_g) of powders to various test surfaces[a]

Powder	Surface	F_{ad} ($\times 10^{-6}$ N)	σ_g
Pregelatinised starch	Chromium nitride	0.30 ± 0.04	0.80 ± 0.03
	Carbon	0.44 ± 0.04	0.81 ± 0.03
	Chromium carbide	0.40 ± 0.04	0.84 ± 0.02
	Plasma-chromium	0.40 ± 0.04	0.82 ± 0.02
	Stainless steel	0.56 ± 0.03	0.87 ± 0.02
Lactose monohydrate	Chromium nitride	0.37 ± 0.02	0.77 ± 0.03
	Carbon	0.57 ± 0.03	0.82 ± 0.02
	Chromium carbide	0.48 ± 0.03	0.84 ± 0.02
	Plasma-chromium	0.45 ± 0.02	0.78 ± 0.02
	Stainless steel	0.99 ± 0.19	0.74 ± 0.02
Calcium carbonate	Chromium nitride	0.53 ± 0.05	0.82 ± 0.02
	Carbon	0.69 ± 0.04	0.82 ± 0.02
	Chromium carbide	0.47 ± 0.02	0.85 ± 0.01
	Plasma-chromium	0.45 ± 0.01	0.84 ± 0.03
	Stainless steel	1.30 ± 0.04	0.80 ± 0.01

[a] Results are the arithmetic mean and S.D. of six replicates.

Table 2
Surface roughness of the test surfaces (results are the arithmetic mean and standard deviation of three replicates).

Surface	R_a (μm)	R_q (μm)	R_{tm} (μm)	FD	β
Chromium nitride	0.22 ± 0.06	0.30 ± 0.00	4.32 ± 0.12	2.66 ± 0.03	113
Carbon	0.25 ± 0.02	0.33 ± 0.02	5.66 ± 0.51	2.61 ± 0.05	96
Chromium carbide	0.23 ± 0.06	0.30 ± 0.01	4.17 ± 0.72	2.65 ± 0.09	107
Plasma-chromium	0.22 ± 0.06	0.30 ± 0.02	4.51 ± 0.36	2.66 ± 0.02	97
Stainless steel	0.19 ± 0.01	0.25 ± 0.00	4.01 ± 0.76	2.45 ± 0.12	123

powder build-up on the pin faces or stickiness to the pin shafts. Lactose monohydrate showed nearly twice the adhesion force to the stainless steel surfaces (Table 1) as pregelatinised starch. Unlubricated lactose monohydrate caused the capsule filling machine to seize up after 25 min. A strongly adhering, sintered powder mass had formed around the ejection pins of the transfer station. A repeat with lubricated powder still showed a slight powder build-up on the pin faces and shafts. The adhesion force to coated surfaces was reduced to a level only slightly but statistically significant larger than that observed using pregelatinised starch (Table 1). In order to avoid damage of the machine, capsule filling using coated pins was undertaken with lubricated lactose monohydrate only. There was visible build-up of powder for the carbon coating. On all other coated surfaces no powder build-up could be seen. The carbon coating was also found to be the least successful in the adhesion measurements for lactose monohydrate. Using calcium carbonate particles, the adhesion force to stainless steel surfaces was greatest in comparison to all the other experiments (Table 1). The use of unlubricated calcium carbonate powder in the capsule filling machine was also difficult. After 10 min the pins were inspected to avoid a seize-up of the machine. It was found that the pins were coated all around with a layer of calcium carbonate. This layer could only be removed with a solution of 10% hydrochloric acid in water. The addition of lubricant did not improve this behaviour. However, in the adhesion studies the use of coated test surfaces indicated a sufficient decrease in the adhesion character of the powder (Table 1). This improvement could also be seen on the coated tamping pins except for the carbon coating. In comparison to lactose monohydrate, however, the general level of powder still sticking to the coated pins indicated that calcium carbonate is rather a troublesome powder. Previous experiments (Hogan et al., 1996) had also indicated that inorganic calcium compounds are less suitable for capsule filling.

From the adhesion measurements (Table 1), the following rank order of adhesion tendency can be formulated for the powders tested: pregelatinised starch < lactose monohydrate < calcium carbonate. Also, for each powder, a rank order of adhesion tendency to the test surfaces can be obtained: chromium nitride < plasma-chromium ≤ chromium carbide < carbon < stainless steel (pregelatinised starch, lactose monohydrate); plasma-chromium ≈ chromium carbide < chromium nitride < carbon < stainless steel (calcium carbonate).

In order to identify the reasons for the above rank order, first the surface roughness of the test surfaces was evaluated. The surface roughness is generally accepted as one of the main factors altering adhesion forces between particles and surfaces due to modification of the true area of contact. For ordinary, but not micronised, powder particles an increased surface roughness was generally found to reduce the adhesion force (Tabor, 1977; Johnson, 1985; Kendall, 1994; Levins and Vanderlick, 1995; Soltani et al., 1995; Maugis, 1996; Podczeck et al., 1996b). A rougher surface provides less asperity tips per unit area and hence fewer contact points with the adhering particles. This results in a decrease in the true area of contact and consequently in a reduced adhesion force. The surface roughness data for the test

Table 3
Surface free energy data (mJ/m^2) of the test surfaces and powders[a]

Surface[b]	γ_s (mJ/m^2)	γ^{LW} (mJ/m^2)	γ^{AB} (mJ/m^2)	γ^+ (mJ/m^2)	γ^- (mJ/m^2)
Chromium nitride	37.99	37.93	0.06	0.00	0.83
Carbon	39.81	38.12	1.68	0.07	9.97
Chromium carbide	34.88	34.14	0.74	0.02	6.12
Plasma-chromium	33.30	32.78	0.52	0.06	1.18
Stainless steel	39.01	37.24	1.77	0.06	13.94
Pregelatinised starch	51.83	43.50	8.33	1.20	14.44
Lactose monohydrate	58.20	43.50	14.70	5.91	9.14
Calcium carbonate	52.37	42.62	9.75	1.64	14.52

[a] The results are based on the arithmetic mean values of ten replicates of contact angle data for three test liquids.

[b] γ_s Total surface free energy; γ^{LW}, Lifshitz–van der Waals term; γ^{AB}, acid–base-interaction term; γ^+, Lewis-acid term; γ^-, Lewis-base term.

surfaces are provided in Table 2. The surface roughness is similar for all the coated test surfaces and, hence, does not offer an explanation for the ranking obtained. The stainless steel surfaces are slightly less rough, which could be one reason for the profoundly stronger adhesion of all powders to this surface material.

Another important factor to consider in adhesion studies is the surface free energy of the powders and the substrate surfaces. 'Like' materials usually adhere strongly (Zimon, 1982). In previous adhesion measurements (Podczeck et al., 1996b) advantage had been obtained from the use of the acid–base interaction concept developed by van Van Oss et al. (1986). This concept allows for the estimation of the contributions of acidic (i.e. electron accepting) and basic (i.e. electron donating) molecules or functional groups of chemicals to the adhesion across an interface. In Table 3, the surface free energy data are summarised for the powders and the test surfaces. Lactose monohydrate and calcium carbonate are Lewis-bases as are the majority of pharmaceutical powders. Pregelatinised starch is amphiphillic, i.e. there will not be a predominant adhesion tendency to the surfaces of Lewis-acid or Lewis-base type (Good, 1992). This could explain why there is only a slight difference in the adhesion force between the coated test surfaces for pregelatinised starch.

The total surface free energy of the test surfaces is similar (Table 3), but the contribution from electron donating surface groups varies greatly. Chromium nitride merely provides a non-polar surface, whereas stainless steel, carbon and chromium carbide surfaces are strong Lewis-bases. Plasma-chromium has only a slight basic character. A ranking of the surfaces on the basis of the Lewis-base values (γ^-) leads to the following order: chromium nitride < plasma-chromium < chromium carbide < carbon < stainless steel. This rank order matches the order of adhesion obtained for pregelatinised starch and lactose monohydrate. Hence, it appears as though the adhesion of the two powders to the test surfaces is governed by their surface free energy properties in line with de Bruyne's rule (Zimon, 1982): The adhesion is strongest to Lewis-base surfaces and at a minimum to surfaces which are different in nature. Using calcium carbonate particles, the above order is interrupted on one occasion, i.e. the chromium nitride surface is displaced: plasma-chromium ≈ chromium carbide < chromium nitride < carbon < stainless steel. Calcium carbonate particles are, as with the majority of inorganic powder particles, very hard. The press-on force applied prior to the adhesion force measurements could therefore have led to a pronounced indentation of the test surfaces, thereby leading to an increase in contact area and hence an increased adhesion force. Harder test surfaces will be indented less and, thus, the increase in adhesion force should be smaller. The literature data indicates that a chromium carbide coating provides a slightly harder surface than a pure metal coating (Hertzberg, 1996). Nitride metal coatings should provide a significantly less hard surface compared to the pure metal coating (Bowden and Tabor, 1954). Consequently, the chromium coatings could be ranked according to their hardness as follows: chromium nitride $\ll$ plasma-chromium $<$ chromium carbide. Taking this rank order into account, the adhesion properties of calcium carbonate can be explained by a combination of hardness and surface free energy properties of the test surfaces. Adhesion is highest to strong Lewis-bases (stainless steel and carbon), whereas the adhesion to moderate Lewis-bases and nonpolar surfaces is governed by the surface hardness. The harder the surface, the smaller is the adhesion force.

The results indicate that the use of chromium coated surfaces (in the form of nitride, carbide or pure metal plasma-coating) would be advantageous for powder filling into hard gelatine capsules by means of a tamp-filling machine. However, it should be borne in mind that the adhesion tests carried out here have been performed on unlubricated test surfaces and unlubricated powder particles. In practice, chromium surfaces are difficult to lubricate (Bowden and Tabor, 1954), which might cause some problems when powder formulations are to be filled over several hours. When using chromium surfaces the lubrication of the powder should therefore be carefully optimised to avoid filling problems.

4. Conclusions

The coating of tamping pins with metal coatings such as chromium nitride, plasma-chromium or chromium carbide can significantly reduce the adhesion of powder particles and, hence, promote powder filling into hard gelatine capsules on tamp-filling machines. In order to identify the best coating centrifugal adhesion force measurements could be undertaken. In addition, surface free energy measurements could also be made to aid identification of the cause of adhesion. A surface finish by means of a chromium nitride coat will provide, in most cases, the best filling conditions. When filling powders containing hard particles, e.g. inorganic excipients, the surface hardness must also be increased. In such cases, a plasma-chromium coat appears best.

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