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QUANTITATIVE EVALUATION OF THE WETTABILITY OF POWDERS

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ABSTRACT

The wetting of powders can be evaluated by different manner : direct measurement of the solid - liquid contact angle ; indirect measurement of that angle (h and ϵ method) ; liquid penetration rate into a powder bed ; a.s.o.

This paper makes a comparison between the different methods, and shows the interest of a photographic technic, which allows the determination of the immediate contact angle.

The wettability of powders is an important property, because wetting is often the first step of dispersion or dissolution. Quick and homogeneous dispersion of a solid in a liquid, and farst dissolution, can only occur when a sufficient wetting is achieved. Thus wettability is a value that should be measured in a quantitative manner in order to appreciate exactly the properties of powders.

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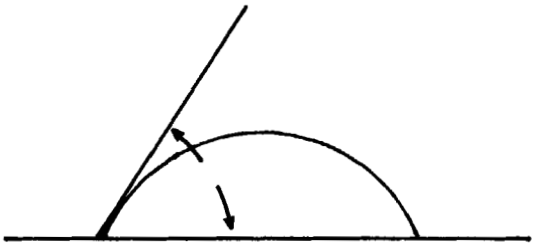

FIGURE 1

Solid liquid contact angle.

Wetting of a solid by a liquid is a surface phenomenon. When a drop of liquid is poured on a solid surface, the wetting of the solid can be appreciated by the contact angle (θ) between the solid and the liquid drop (figure 1).

If the value of θ is near by zero, the wetting is called perfect. If θ is highter than 90°, the powder is not wetted (figure 2). So a good measurement of the contact angle gives a precise and quantitative idea of wetting.

Wetting is also an important factor in the rate of penetration of a liquid into a powder bed.

According to WASHBURN[15], a tablet can roughly be considered as a powder bed in which are small capillars of constant radius R. If this is the case, the penetration rate of a liquid into the powder is given by the equation :

$$L^2 = \frac{R.\gamma.\cos\theta.\ t}{2.\eta}$$

called WASHBURN equation, where
L is the lenght of liquid penetration

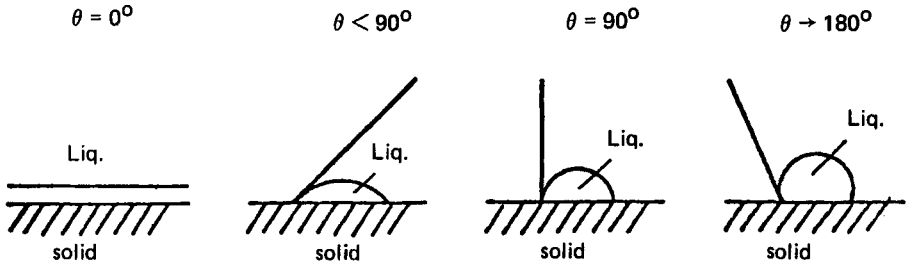

FIGURE 2
Wetting of a solid by a liquid.

R the capillar radius
γ the liquid surface tension
θ the contact angle
t the time
η the liquid viscosity.

This relationship between the length of penetration and the time is only verified when the powder bed is homogeneous, and its structure can be kept unchanged during all the experiment (no dissolution should occur).

If these conditions are verified, the WASHBURN equation can be used to calculate the contact angle.

1. PREVIOUS WORKS

There are various methods described by several authors to measure the value of θ : Some of them try to measure directly the value of θ (for example by measuring the height and the width of the drop) ; others use indirect determination for θ .

1.1. Direct measurement of contact angle

HARDER[6] and WOOD[16] have described a direct measurement method of the contact angle by use of a telemi-

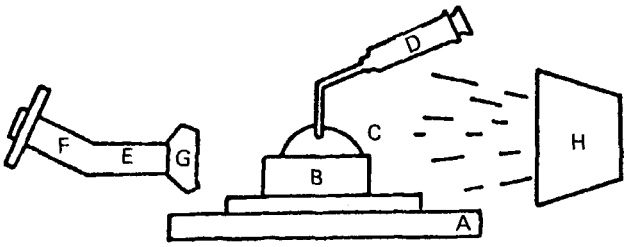

FIGURE 3

Apparatus used for a direct measurement of contact angle
A : shelf. B : powder bed. C : liquid drop. D : syringe.
E : telemicroscope. F : eyepiece. H : light.

croscope (figure 3).

The observation of the magnified drop shape allows a direct evaluation of the contact angle. The authors pour a drop on the powder, and then measure the contact angle ten times (one measurement every ten seconds). Each experiment is made on ten different powder beds, so that the values of contact angle given by these authors is the mean value of one hundred of measurements.

In his work, HARDER[6] studied the relationship between the contact angle and the surface tension of two kind of wetting liquids. He prepared mixtures, in various proportions, of methanol and water or butanol and formamide, and measured the contact angle of these liquids with acetylsalicylic acid tablets : This authors obtained a staight line relation between the contact angle and the surface tension (figures 4 and 5), but the slope of the line obtained with water methanol mixtures was highter than that observed with the butanol formamide mixtures. This shows that wetting depends not only on the surface tension of liquid.

ERHARDT[4] used an other method to measure the con-

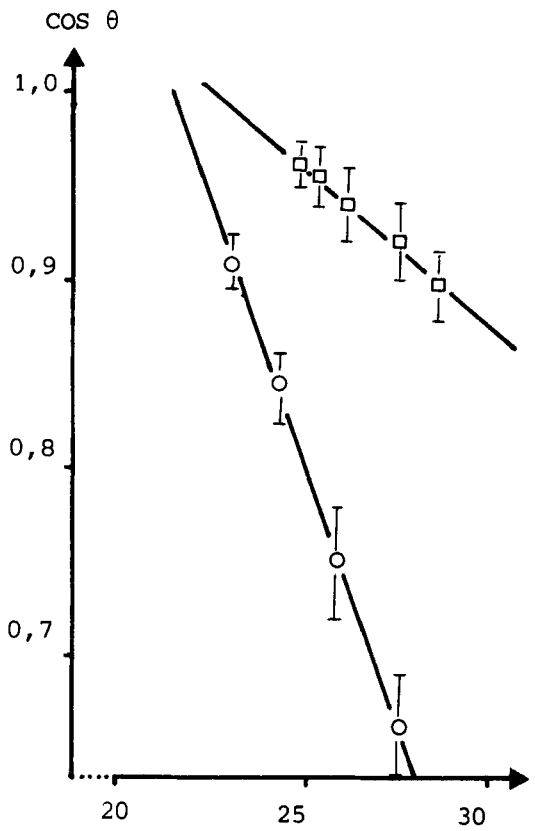

FIGURE 4

Acetylsalicylic acid tablets containing 1 % of magnesium stearate

O methanol-water mixtures

□ butanol-formamide mixtures.

tact angle (figure 6) : a projection apparatus allows a magnification of the picture of the drop. With a micrometer, the height and the radius of the drop are measured on the screen, and the value of θ calculated. By this method, ERHARDT tried to realise an optimisation of the formula of coating solutions. He studied the influence of various solvants, pigments and tablet porosity on the value of θ .

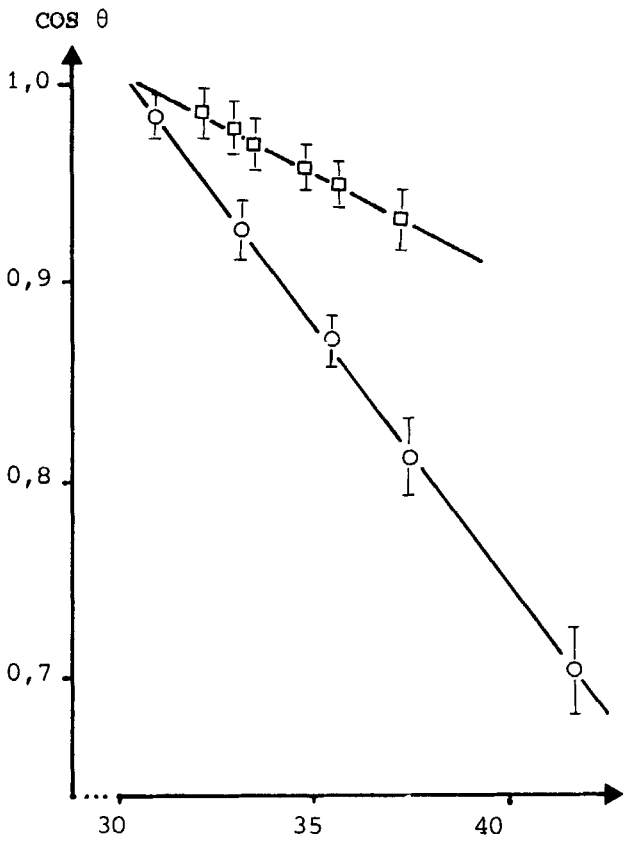

FIGURE 5

Acetylsalicylic acid tablets containing 1 % of talc
O methanol-water mixtures
□ butanol-formamide mixtures.

COUVREUR[3] also used a similar technique. He measured the contact angle and the pore radius in order to calculate, by mean of the WASHBURN equation, the liquid penetration lenght of a disintegration liquid into various tablets containing starches. By this way, the author reported that tablets showing good disintegration properties show also hight penetration lenght values, and those having bad disintegration properties show small or even negative penetration length values.

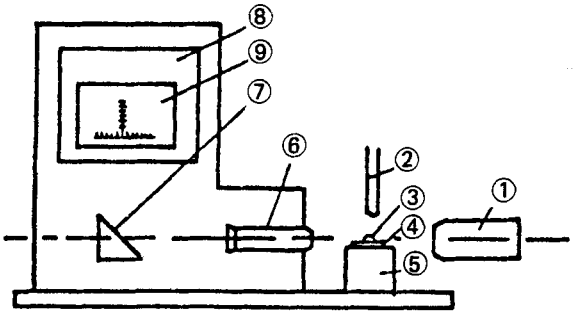

FIGURE 6

Apparatus used by EHRARDT (4)
1 : light. 2 : syringe. 3 : liquid drop. 4 : powder bed.
5 : shelf. 6 : lens. 7 : miror. 8 : screen. 9 : micrometer.

More recently, VAN BRACKEL[1] measured the contact angle of liquids having various surface tensions. His experiments were conduced on polystyrene, polyethylene and glass. They allowed him to propose various hypothesis upon wettability. These works showed that wetting is not a simple phenomenon which can be described by a small number of equations.

1.2. Indirect methods

1.2.1. Washburn method

The indirect methods are almost based on the WASHBURN equation.

WASHBURN described a method using a glass tube. A given amount of powder is poured into the tube on a cotton stopper. The powder is taped to densify it, and the lower end of the tube is brought in contact with the wetting liquid, so the height in the tube can be mesured as a function of time, and the contact angle calculated.

SAMALIGY[13] used the same kind of method in order

to study the influence of surfactants like polysorbate 80 or sodium laurylsulphate on the wetting of magnesium silicate. This author reported, for each surfactant, an optimum concentration value for wetting. This value is not the same for each surfactant, and there is no correlation between wetting and the HLB value of the surfactant. The same study, done with silicon dioxide as a solid showed a difference of behaviour with non ionic surfactants. The author explained the difference by an other orientation of the hydrophilic part of the surfactant on the powder surface.

NOGAMI[12] also used a kind of WASHBURN method : on a special experimental apparatus, described by the author, he studied the penetration length as a function of the porosity of powders. He noticed an increase of the penetration length with the degree of tapping, the fluid temperature and the humidity of the powder.

NOGAMI also studied the influence of the fluid viscosity : he showed that the penetration rate of water solutions diminishes when the viscosity increases.

GANDERTON[5] used an other kind of method : his experiments were done with an U tube filled with cyclohexane. At one end of the tube, he put a tablet, and measured the absorption rate of the liquid by measuring the withdrawal of the liquid in the other part of the U tube. He studied with this method the influence of magnesium stearate concentration on wetting of tablets.

STUDEBACKER[14] used approximately the same method as SAMALIGY to quantify the contact angle : When a liquid is perfectly wetting a solid $\theta = 0$. The WASHBURN equation becomes then :

$$L^2 = \frac{\gamma' . r . t'}{2 \eta'}$$

With a liquid whose wetting properties are bad

$$L^2 = \frac{\gamma''.\cos\theta\ ''.r.t''}{2\,\eta''}$$

Dividing the two relations by one another :

$$\cos\theta\ '' = K \cdot \frac{t'}{t''}$$

So the measurement of the contact angle can be simply realised by measuring the time necessary for a perfect and non perfect wetting liquid to penetrate a given length into the powder bed.

1.2.2. h and ε method

This method was described by KOSSEN and HEERTJES[8,9] It is based on the hypothesis that powder are constituted of spherical particles having the same diameter. When such a powder is compressed into a compact bed, and the bed saturated with a liquid, the powder is completely immerged in the liquid, excepting the spherical top of the particles placed at the upper face of the powder bed. To measure the contact angle, a drop of liquid (which must be a saturated solution of the solid) is deposit on that surface, and its height (h) measured. From this height, the contact angle can be calculated using two kind of equations :

1°) If $0° < \theta < 90°$

$$\cos\theta = 1 - \sqrt{\frac{1}{3(1-\varepsilon)\ (1/Bh^2 - 1/2)}}$$

2°) If $\theta > 90°$

$$\cos\theta = -1 + \sqrt{\frac{2}{3(1-\varepsilon)}\ (2/Bh^2 - 1)}$$

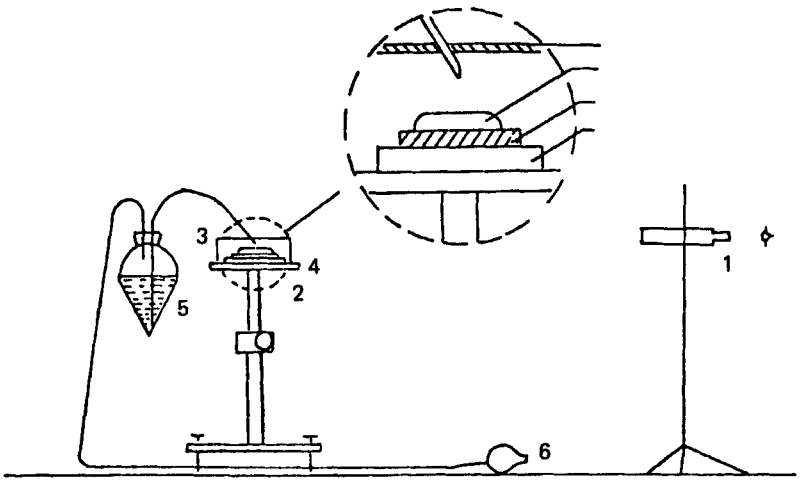

FIGURE 7

Apparatus used for the measurement of the drop height.
1 : telemicroscope. 2 : shelf. 3 : measuring cell.
4 : powder bed. 5 : liquid reservoir.

where $B = \rho_1 \cdot g/2$

h = height of the drop

ρ_1 = density of the liquid

g = acceleration due to the gravity

ε = porosity

The height of the drop should only be measured when the volume of the drop is so great that any addition of a droplet of liquid does not increase the height of the drop.

The cos θ determination by the $(h - \varepsilon)$ technique should only be achieved on large compacts of powders. The apparatus used by KOSSEN and HEERTJES is shown in the figure 7.

LERK[10,11] used the same method in order to calculate the contact angle of many powders. He especially

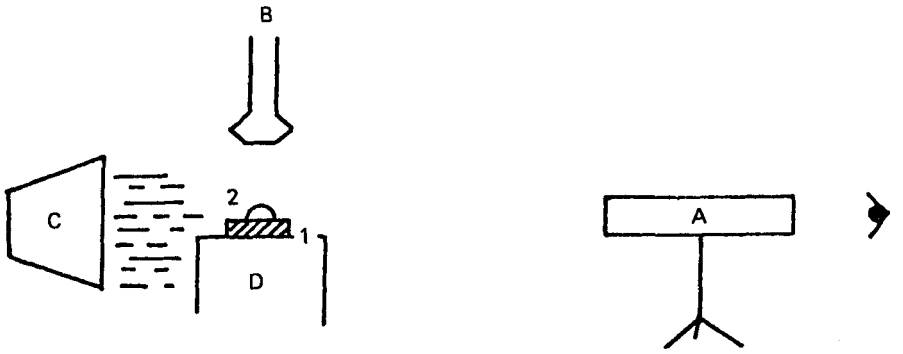

FIGURE 8
Measurement of the height and diameter of the liquid drop (direct measurement).

studied the influence of particle size on wetting, and reported that the contact angle diminishes when the particle size decreases.

HERTJES and KOSSEN[7] compared the (h and ϵ) technique with that of WASHBURN, and concluded that their method is more accurate and more reproducible.

Remark : The wetting can also be quantified in a certain manner without determination of the contact angle. It is possible to measure the speed of immersion of a given amount of powder into liquids having various surface tensions. From this speed a wetting coefficient can be calculated.

2. PERSONAL WORKS

In order to check which kind of method gives the best results, a comparison of different techniques was undertaken.

2.1. Direct measurement of the contact angle

For this kind of measurement a method similar to that described by EHRHARDT (figure 8) was used : the tablet (1) is put on the shelf (D) where it can be ligh-

TABLE 1 : Contact Angle of Various Products.

Product	Contact angle	Standart deviation	Contact angle given by LERK
Dicalcium phosphate	0°	0 %	0°
Lactose	10°	67 %	30°
Coffein	34°	14 %	43°
Aspirin	59°	10 %	75°
Salicylic acid	68°	10 %	103°
Potassium chloride	17°	38 %	21°

tened (C). When the liquid drop (2) is poured on the tablet surface, the length of the drop is measured by the telemicroscope (A) and its diameter by the magnifing glass (B). So the contact angle could be calculated. The mean values of ten measurements are given in table 1, where are also reported the contact angle values published by LERK[10,11].

The experimental values are not always in the same range, expecially with powders having high contact angle values (aspirin, salicylic acid). These differences can be explained by the bad reproducibility of the measurements (standart deviations are given in table 1). The poor reproducibility is probably due to two kind of reasons :

- the height of the drop should be measured quicker than possible with the telemicroscope ;
- the drop diameter is over evaluated when the

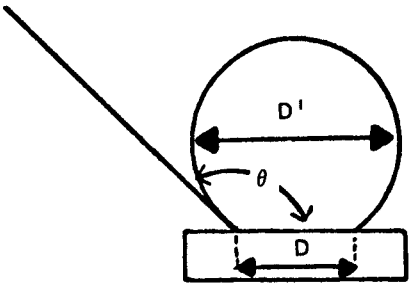

FIGURE 9

Difference between the projected diameter and the true diameter of a liquid drop.

contact angle is greater than 90°, because the magnifing glass is located above the drop, so the projected diameter (D') is read instead of the real diameter (D) (figure 9).

The direct measurement seemed, for theses reasons, not to be a suitable technique.

2.2. h and ε method

In these experiments, several drops of liquid poured on the surface of the tablet, in order to form a big drop, whose height is constant. Then the contact angle value was calculated. The results of these experiments are reported in table 2.

This method seems to be reproducible, and the found values are similar to those given by the litterature. But a problem arises when contact angle have to be measured on powders which absorb quickly the liquid : during the time taken by the measurement, the contact angle may change, because the liquid penetrates into the tablet, even if the tablet has been saturated with liquid before the experiment, so that the measured contact is not always the true contact angle, but a con-

TABLE 2 : Contact Angles Measured with the h and ε Method.

	Contact angle	Standart deviation	Value given by LERK
Aspirin	73°	1.6 %	75°
Potassium chloride	31°	2.8 %	21°

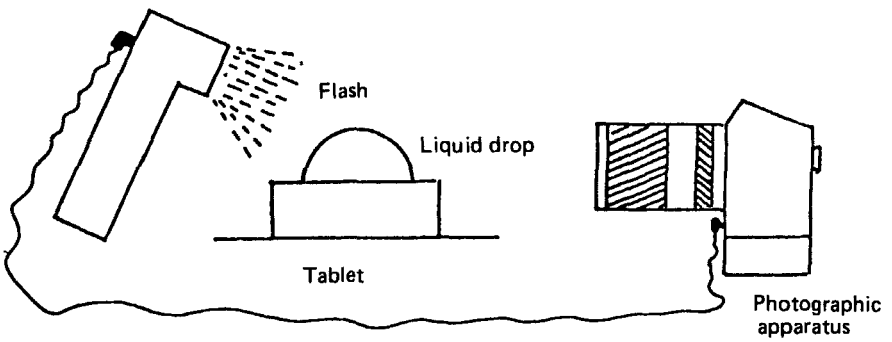

FIGURE 10

Photographic method.

tact angle after penetration.

2.3. Photographic method

In order to measure instantaneously, and precisely the real contact angle, a photographic method was used (figure 10).

The shape of the drop is photographied immediately after it is poured on the tablet by a motorized photographic apparatus. This method also allows to follow the contact angle value as a function of time.

The results obtained with this method were compared with the data given by the h and ε method. All

TABLE 3 : Characteristics of Wetting Liquids

Product	Solid density (g/cm^3)	Saturated water solutions (23°C) Surface tension (dynes/cm)	Density (g/cm^3)
Aspirin	1.35	48.2	0.999
Paracetamol	1.26	51.1	1.001
Phenacetin	1.16	59.2	0.998
Potassium chloride	1.94	53.0	1.174

these experiments were achieved on large diameter (50 mm) compacts ; each compact was wetted with a saturated solution before measuring the contact angle. The characteristics of the wetting liquids are given in table 3. For each product, two serials of five photographies were taken after saturation of the tablet by the wetting liquid :

-the first serial is a photography of the first drop

- the second serial is a photography of the drop of maximal height.

The results of these experiments are given in table 4. These results show that, when the contact angle is calculated with the h and ε method, the obtained values are near by those published by LERK. But the values are different when they are directely measured on the photography (first drop). On the other side, the values are different when the first drop or the maximal height drop are taken.

The influence of the surface tension of wetting liquid was investigated at the same time as the repro-

TABLE 4 : Comparison between the Direct Photographic Method, the h and ε Method and the Values given by the Litterature (Key : F = first drop; M. = drop of maximal height).

Product	Porosity ε	Drop height (cm)	Contact angle		
			Direct measurement	Calculated by h-ε method	Given by LERK
Aspirin	0.0553	F. 0.161	55°	57°	-
		M. 0.244	52°	72°	73°
Paracetamol	0.0368	F. 0.100	25°	42°	-
		M. 0.161	33°	54°	59°
Phenacetin	0.0859	F. 0.182	66°	56°	-
		M. 0.337	67°	80°	78°
Potassium chloride	0.0098	F. 0.058	13°	33°	-
		M. 0.072	11°	36°	21°

TABLE 5 Surface Tension of Water - Isopropanol Mixtures

Surface tension (dynes/cm)	Isopropanol quantity mixed for 100 ml water
24.7	75
28.7	30
29.9	27.5
34.9	18
39.5	13.5
45.6	8
50.7	5
55.7	3
58.5	2
62.3	1.5
69.3	0

TABLE 6 : Influence of the Surface Tension on the Contact Angle and Reproducibility of the Method.

Surface tension (dynes/cm)	Contact angle of griseofulvin		Contact angle of stearic acid	
	Mean value	Standart deviation	Mean value	Standart deviation
24.7			19°	3°
28.7			24°	2°
29.9	20°	2°	35°	3°
34.9			42°	5°
39.5	28°	5°	57°	3°
45.6	32°	2°	63°	3°
50.7	38°	4°	66°	6°
55.7			79°	3°
58.5	36	5°		
62.3			83°	3°
69.3	46°	2°	90°	2°

ducibility of the photographic method. For that purpose, isopropanol and water were mixed in various proportions in order to obtain various surface tensions (table 5), and the mixture was used to wet tablets of stearic acid and of griseofulvin. The observed values are given in table 6 (mean values of ten measurements). They show a good reproducibility of the method.

The variation of contact angle as a function of surface tension is indicated in figure 11. It shows how important it is to take the liquid surface tension into account in the contact angle determination.

The different methods described by the litterature need a certain time to achieve the measurement of con-

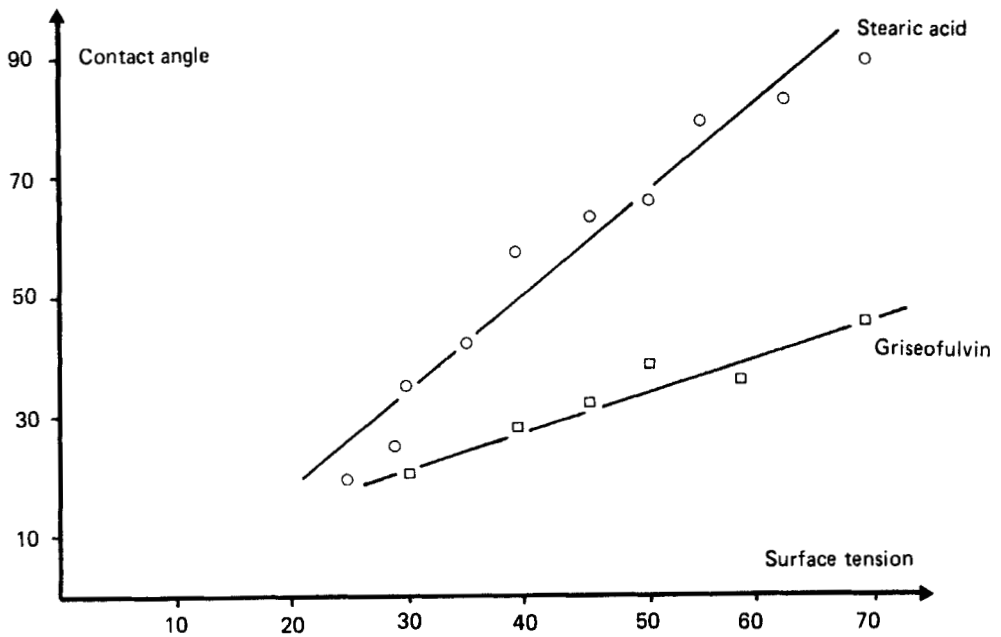

FIGURE 11

Contact angle variation as a function of wetting liquid surface tension.

tact angle. Thus several authors measured the contact angle after a definite time : for example COUVREUR[3] measured the angle after 30 seconds. ZOGRAFI[17] measured it after 5 minutes.

It seemed interesting to follow the variation of the contact angle as a function of time, by taking photographies at different times after the deposit of the liquid on the solid. The results observed with aspirin, phenacetin, potassium chloride and paracetamol are reported in table 7 : In every experiment, the contact angle value decreases during the time. The speed of this decrease if function of several factors (solubility of the compact, height of the drop, porosity a.s.o.). The calculation according to the h and ε method (also reported in table 7) gives some more constant results than the direct observation of the drop. It seems how-

TABLE 7 : Contact angle variation as a function of time.

	Porosity ε	Time seconds	First drop height (cm)	Contact angle	
				Direct measurement	Calculated (h and ε method)
Aspirin	0,0373	0	0,1528	53	49
		30	0,1174	36,5	42
		60	0,1156	37	42
		90	0,1119	33,5	41
		120	0,1115	32,5	41
		180	0,1110	32,5	41
		240	0,1092	32	41
		300	0,1060	32,5	40
		600	0,0977	29	38
		900	0,0904	27,5	37
Phenacetin	0,0606	0	0,1477	52	49
		30	0,1468	50,5	49
		60	0,1454	50	49
		90	0,1454	48,5	49
		120	0,1454	48,5	49
		180	0,1394	48,5	48
		240	0,1380	47	48
		300	0,1329	45,5	47
		600	0,1218	40,5	46
		900	0,1083	38	42
Potassium Chloride	0,0209	0	0,1139	28	43
		30	0,1032	27	41
		60	0,0968	25,5	39
		120	0,0959	25	39
		180	0,0905	23	38
		240	0,0793	22,5	35
		300	0,0752	20,5	35
		600	0,0523	13,5	29
		900	0,000	0	0
Paracetamol	0,1123	0	0,1195	35	45
		10	0,0620	18	32
		20	0,0355	9	24
		30	0,0326	7,5	23
		40	0,000	0	0

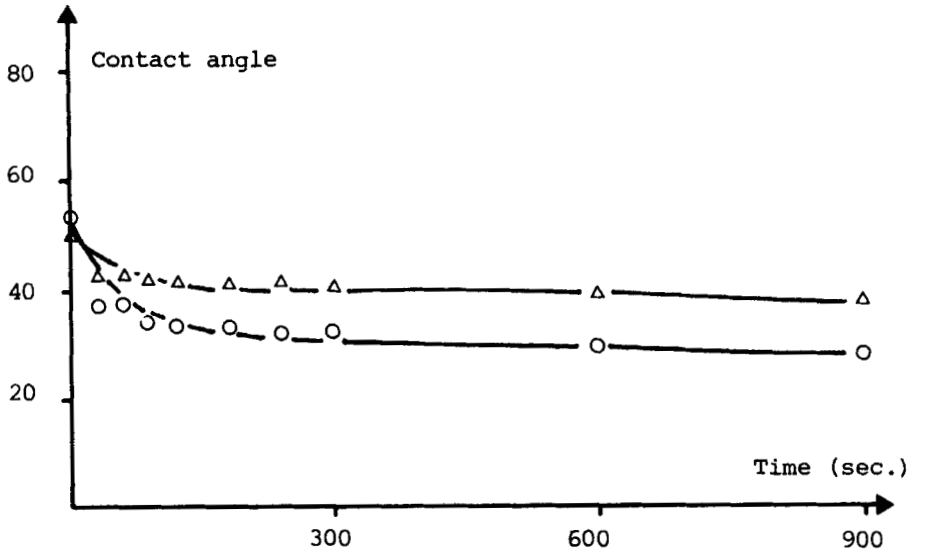

FIGURE 12

Aspirin/water contact angle variation as a function of time (O : direct measurement - Δ : h and ε calculation).

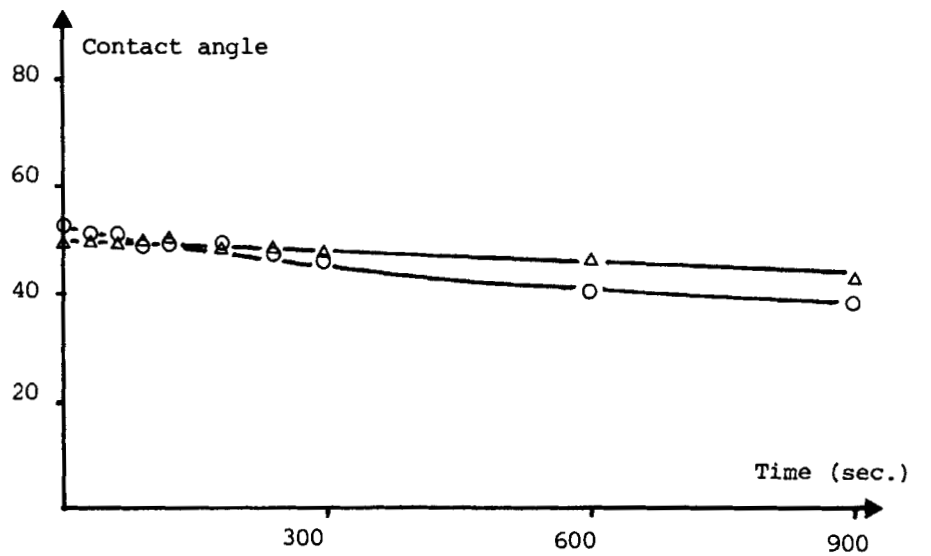

FIGURE 13

Water - phenacetin contact angle variation as a function of time (O : direct measurement - Δ : h and ε calculation).

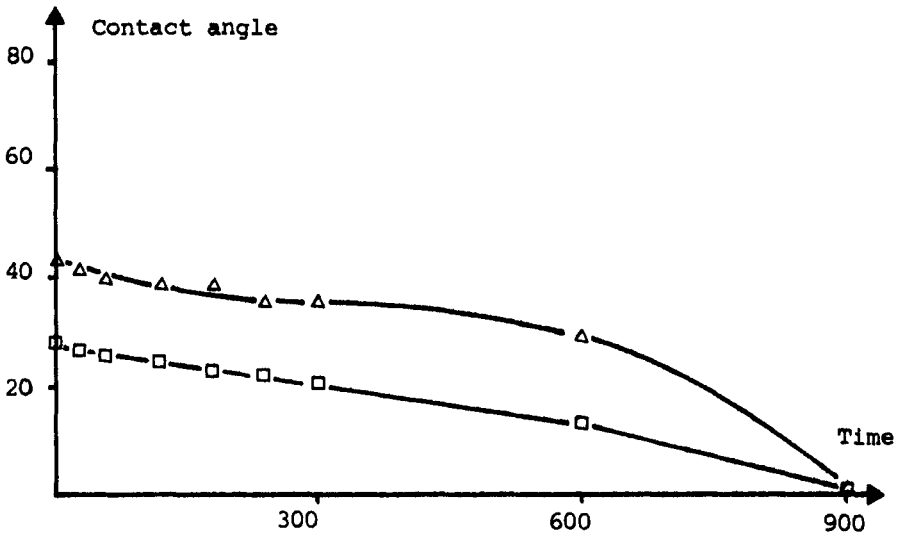

FIGURE 14

Water - potassium Chloride contact angle variation as a function of time (key : O = direct measurement - Δ = h and ε method).

ever that in no case the contact angle becomes stable after five minutes. These results are also given in figures 12, 13, 14 and 15. The experimentation shows how important it is to measure the contact angle immediately after the deposit of the drop of liquid. The variation of the contact angle can also be shown in the case of tablets containing dicalcium phosphate (EMCOMPRESS) lubricated with 1 % of magnesium stearate and containing various amount of potatoe starch as a disintegrant (figure 16) : At the beginning of the experiment, the contact angle of all the tablets is the same (102°), but after a few seconds, the height of the drop decreases in the case of tablets containing 10 or 20 % starch, so that the apparent contact angle is lower.

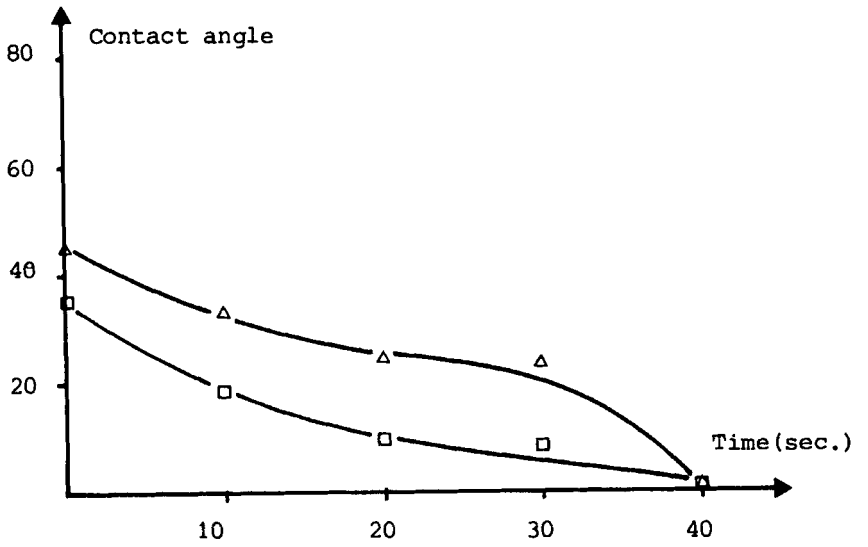

FIGURE 15

Water - paracetamol contact angle variation as a function of time (key : O direct measurement - Δ = h and ε calculation).

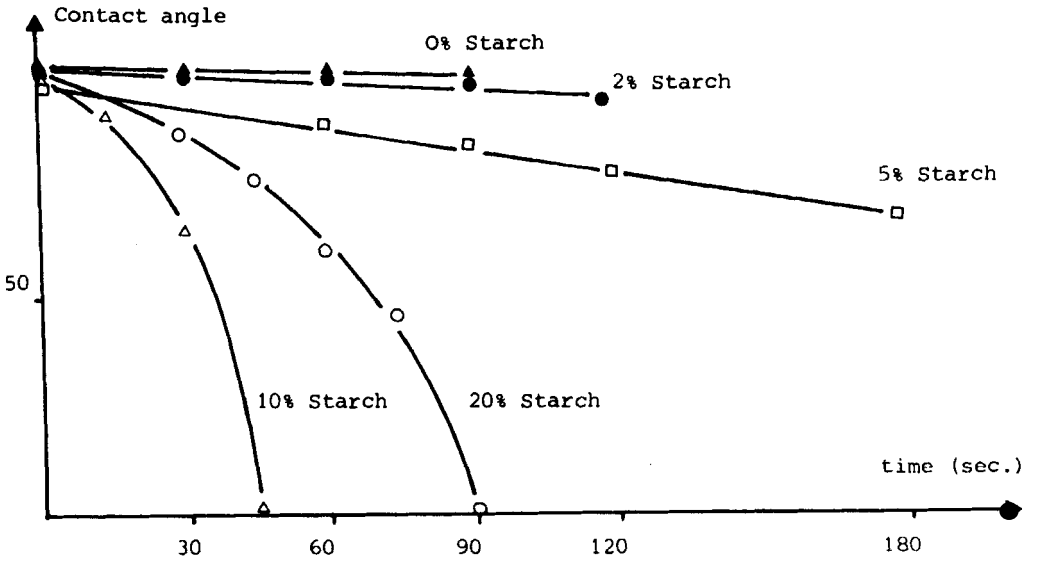

FIGURE 16

Variation of the contact angle between water and dicalcium phosphate - starch tablets as a function of time.

FIGURE 17

Apparatus for the measurement of penetration length (key : 1 = liquid drop - 2 = powder bed - 3 = liquid deposit device - 4 = telemicroscope).

2.4. Indirect method (penetration length)

In order to see if the measurement of penetration length of liquid in tablets allows, using the equation of WASHBURN, a good calculation of the contact angle, it was tried to measure the volume of liquid absorbed by powder beds in an apparatus similar to this described by NOGAMI[12]. An other method was also used to follow directly the liquid penetration, using a telemicroscope (figure 17). The two kind of methods gave comparable results. The results are reported in table 8. The calculation of the contact angle needs the knowledge of different factors :

$$\cos \theta = \frac{2 \cdot L^2 \cdot \eta}{r \cdot \gamma \cdot t}$$

where L is the liquid penetration length

η is the liquid viscosity

r is the pore radius in the powder bed

γ is the surface tension of the wetting liquid

t is the time

TABLE 8 : Penetration Length of Various Liquids in Dicalcium Phosphate Tablets Containing 5 % of Potatoe Starch and 1 % Magnesium Stearate.

Time (sec)	Penetration length (cm) of Benzene	Propanol-2	Butanol	Ethanol
0	0	0	0	0
15	0,17	0,123	0,144	0,176
30	0,24	0,216	0,197	0,255
45	0,29	0,269	0,229	0,289
60	0,317	0,310	0,275	0,315
75	0,358	0,328	0,3	0,326
90	0,383	0,357	0,332	0,348
105	0,433	0,388		0,362
120	0,440	0,424	0,373	0,387
135		0,454	0,415	0,422
150			0,445	0,442

TABLE 9 : Comparison between the Penetration Length evaluated with Different Methods.

Time sec	L.calculated with r obtained by permeametry (cm)	L calculated with r obtained with the Ganderton method (cm)	Experimental value of L (cm)
0	0	0	0
15	1,59	2,83	
30	2,25	4,00	0,11
45	2,75	4,90	
60	3,18	5,66	0,23
120	4,50	8,00	0,33

The viscosity and the surface tension of the liquid can be known, but a problem arises in the determination of an average value of the pore radius r.

A permeability method, based on the Kozeny Carman equation has been used, as also the equation given by GANDERTON[5]. In the case of ethanol, the wetting of tablets is perfect, and the θ value, observed directly, is equal to zero. So the different values are :

$$\cos \theta = 1$$
$$\eta = 1.19 \times 10^{-2} \text{ poises}$$
$$\gamma = 22.8 \text{ dynes /cm}$$

With these values, and the average pore radius, the theoretical penetration length has been evaluated, and compared with the experimental value (table 9).

It can be seen than the values are quite different.

In order to verify if these differences are due to a bad measurement of the pore radius or to a poor appli-

TABLE 10 : Penetration Length of Benzene and Alcohol

Time (seconds)	L benzene (cm)	L^2 benzene (cm^2)	L alcohol (cm)	L^2 alcohol (cm^2)
30	0.24	0.058		
60	0.31	0.096	0.23	0.053
90			0.33	0.109

cation possibility of the Washburn equation to tablets, the length of penetration of benzene and ethanol were especially studied. A part of the results are given in table 10.

The two liquids show a contact angle equal to zero. So taking penetration times which give the same penetration length (benzene 30 sec and alcohol 60 sec. or benzene 60 sec. and alcohol 90 sec.) there should be a precise proportionnality between γ, η and t, because the radius r is constant (the same tablets were taken for the two experiences), and the contact angle is zero.

The results should show that :

$$\frac{\gamma \text{ benzene}}{\eta \text{ benzene}} \times 30 = \frac{\gamma \text{ alcohol}}{\eta \text{ alcohol}} \times 60$$

and

$$\frac{\gamma \text{ benzene}}{\eta \text{ benzene}} \times 60 = \frac{\gamma \text{ alcohol}}{\eta \text{ alcohol}} \times 90$$

This theoretical proportionnality could not be verified, and so the Washburn equation seems not to be strictly applicable to tablets. This could be explained by the fact that the Washburn equation has been esta-

blished on an ideal capillary model, and in tablets there are pores with various radius and with a big tortuosity factor.

CONCLUSION

This paper studied several methods for measuring the contact angle between a solid and a liquid.

A photographic method seems to give good and reproducible results. This method is simple, and allows an easy storage of the experimental results.

It shows that the value of contact angle changes during the time, and underlines how important it is to measure the contact angle at the beginning of the experiment.

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