INFLUENCE OF DROP VOLUME ON TIME - DEPENDANT CONTACT ANGLE

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Abstract: *The wetting properties of nonprinting and printing areas on a lithographic printing plate have a key role for achieving high quality printing properties. Measurement of contact angle is one of the most commonly used methods in determination of wetting properties of a solid. There are many parameters which could influence contact angle value. Aim of this paper was to investigate influence of time and drop volume on contact angle value. The wetting characteristics of printing and non-printing areas of the offset printing plates were defined by measuring the spreading contact angle of standardized liquids. Measurements of the static and dynamic contact angles were made with various drop volumes. Results have shown that contact angle values and consequently surface free energy values of non-printing areas (polar characteristics) have been significantly changed depending on the time period of measurement and drop volume. This research has also proved that drop volume has significant influence on both static and dynamic contact angle value.*

Key words: *dynamic contact angle, wetting, surface free energy, printing plate*

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1. Introduction

Among various surface analytical methods available, determination of the contact angle and wettability properties remain as a standard methods for characterisation of the different surfaces (Lander et al., 1993). By determination of contact angle between the defined liquids and certain surface it is possible to get the wetting properties of the solid surface, information about the homogeneity and roughness characteristics of the surface, information about the interaction between the liquid and the solid. These kind of measurement fall into the tensiometry area, where the contact angle is defined through the interfacial energy of the solid-liquid, liquid-vapour and solid-vapour interfaces (Hamraoui, et al., 2000). In most situations equilibrium state is hardly to reach, which leads to the fact that precise description of the wetting characteristics becomes quite complex. On the other hand, the information of the contact angle depends on the speed and direction of movement of the liquid droplet on the surface. These facts point out that characterization of wetting properties of surfaces is highly complex and that absolute results are hard to achieve.

Previously, the contact angle was measured and results of these measuring were published under the assumption that the droplet of the liquid rests on a solid surface (static contact angle). Information about contact angle was useful for the liquid droplets whose shape stabilises immediately after attaching to a solid surface.

The aim of this paper was to determine which changes occur in the liquid droplets on printing plate surfaces when the contact angle is changed over time (dynamic contact angle) (de Ruijter, 1998) and the influence of drop volume on contact angle value. The speed of spreading depends on a combination of several factors, and can be understood from variations in the contact angle over time (Fig. 1).

Fig. 1. Changes of the contact angle with time function

Results obtained in this paper will be useful for two reasons. The first one will be useful in offset reproduction where the functionality of the printing plate depends on the fountain solution and printing ink adsorption. The second goal is directed to easier determination of contact angle and possible standardization of the measurements based on goniometry principles.

2. Information

Aluminium surface suitable for use as an offset printing plate consists of two different areas: ink-receptive image areas which carry a photosensitive coating and fountain solution-retaining non-image areas. In order to improve the fountain solution adhesion on the aluminium oxide film and to enhance the adhesion of the photosensitive coating during the printing process the foil is roughened by electrochemical graining and anodic oxidation (Dimogerontakis et al., 2006; Limbach et al., 2003). During the printing process, printing plates are first covered with fountain solution which has to be adsorbed on non-printing areas (aluminium-oxide), and afterwards is covered with printing ink which is then adsorbed on the printing areas (photosensitive coating).

3. Experimental

Video based, optical contact angle measurement was performed by DataPhysics OCA30 device. It ensures the static and the dynamic characterization of liquid/solid interfaces by contact angle measurement procedure, the requirement for the calculation of surface free energy. In this paper contact angle was measured by using the sessile drop method and surface free energy were calculated by using Owens-Wendt-Rabel and Kaelble (OWRK) analysis method (1) (Dörfler).

$$\gamma_l = \gamma^d{}_l + \gamma^p{}_l \quad (1)$$

$$\gamma_s = \gamma^d{}_s + \gamma^p{}_s \quad (2)$$

where γ_l and γ_s are the surface free energy of liquid and solid respectively, γ^d is the dispersive and γ^p the polar components of the surface free energy (surface tension).

Wetting properties of non-printing and printing areas of printing plates were calculated by measuring the contact angle of three liquids of known surface free energy and viscosity (Tab. 1) (van Oss et al., 1993). Contact angles of liquids were defined from average values of seven liquid droplets placed on different areas of the same printing plate sample. Contact angles of liquids were calculated after 0.2s, 0.4s, 0.6s, 1.0s and 2.0s of droplet relaxation.

All measurement were the made with various volumes of liquid drop, water and glycerol from 0.5 to 5 µl with step of 0.5 µl and diiodomethane from 0.6 to 1.5µl (step of 0.1 µl) as this is the highest volume of diiodomethane before gravitation force is higher than surface tension which causes release of the drop from needle before contact with printing plate surface.

Liquid	Surface free energy γ (mNm^{-1})			Viscosity (mPas)
	γ_{lv}	γ_{dlv}	γ_{plv}	
Diiodomethane (Ström)	50.8	50.8	0.0	2.78
Glycerol (van Oss)	64.0	34.0	30.0	1412
Water (Ström)	72.8	21.8	51.0	1.002

Tab. 1. Surface free energy (γ_{lv}) and their dispersive (γ_{dlv}) and polar (γ_{plv}) components and viscosity of liquids

Printing plate samples were prepared to the standardized processing procedure. The samples were exposed for 75s and chemically processed in NaOH solution at the temperature of 24°C (pH=12.68; χ=8.35 $mScm^{-1}$) as photoactive coating becomes soluble in alkaline solution by light irradiation (Shriver&Atkins, 1999).

4. Results and discussion

4.1 Results of time dependant contact angle measurement

In Fig. 2 results of the relative contact angle measured on the printing areas are presented. One can see that there is a small difference in contact angle values of glycerol during the time period. The values of contact angles measured with water and diiodomethane on mainly dispersive solid surface do not change in time. This could be the consequence of their surface free energies while these two liquids are mainly dispersive (diiodomethane) or polar (water).

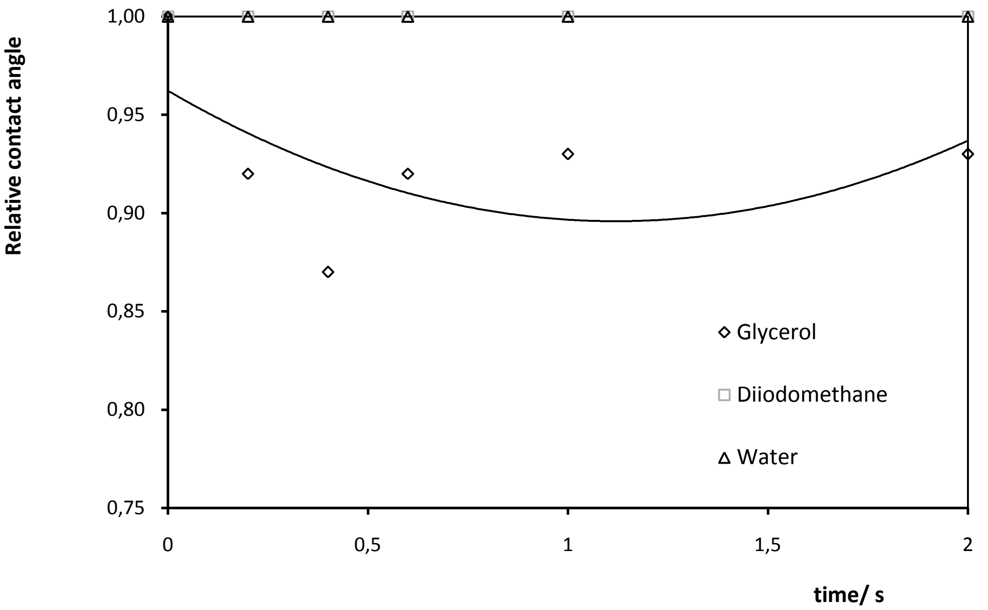

Fig. 2. Relative change of contact angle on printing areas during the time period

Higher difference can be seen on mainly polar surface (non-printing areas). Results are shown in Fig. 3. Significant changes of contact angle values depending on measured time can be seen. On mainly dispersive solid surface (printing areas) only glycerol has shown lowering of contact angle values while on polar surfaces all samples have shown decreasing of values during the time. The highest decrease is occurred by diiodomethane, it has the smallest surface free energy (Tab. 1). On the other hand, the smallest decrease is measured by glycerol which is probably the consequence of its higher viscosity (Tab. 1).

Results of the surface free energy calculation can be seen in Fig. 4. It can be seen that these results are in correlation with results shown in Figs. 2 and 3. The value of surface free energy of printing areas is not significantly changed during the time, as only one factor in its calculation has been changed. On the other hand, on non-printing areas (polar) the value of surface free energy has changed notably, increasing its value for nearly 30%.

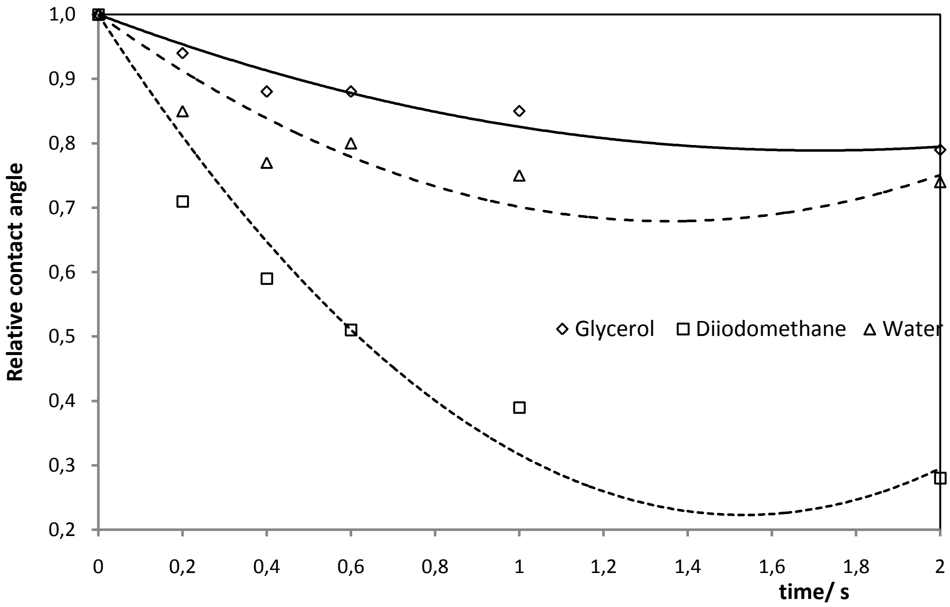

Fig. 3. Relative change of contact angle on nonprinting areas during the time period

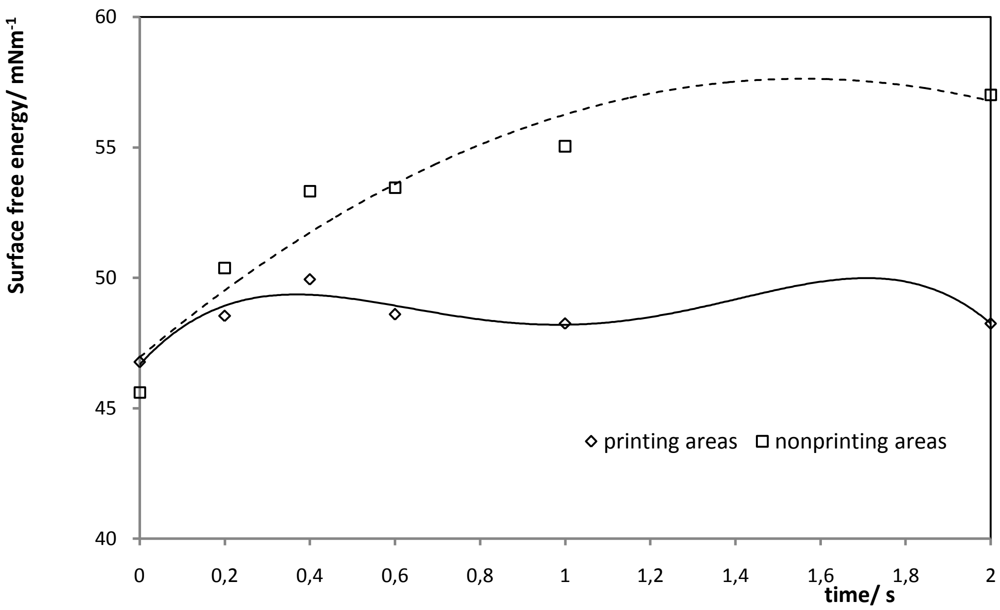

Fig. 4. Surface free energy depending on contact angle dynamics

4.2 Results of volume dependant contact angle measurement

In Figs. 5 to 7. one can observe behaviour of the contact angle values when varying liquid drop volume and influence of the drop volume on the time dependant contact angle measured on the printing (left)and nonprinting (right) areas of the printing plate.

One can see that increasing drop volume causes increase of the contact angle values innearly all investigated surfaces and liquids.

Contact angle of glycerol is higher on the nonprinting areas than on the printing areas of the printing plate. As said before printing areas are built of photoactive coating which is mainly dispersive surface and therefore attract dispersive liquids better than a polar surface. The influence of the drop volume is higher at printing areas (Fig. 5 left), where difference between minimal and maximal measured value is round25 % while on the non printing areas (Fig. 5 right) is that difference under 15 %.

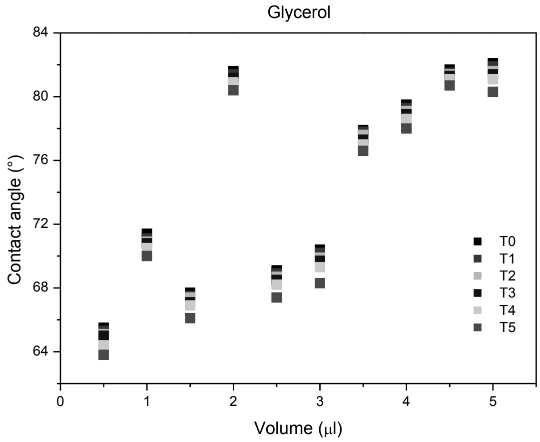

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Fig. 5. Contact angle value depending on drop volume of glycerol on printing areas (left) and nonprinting areas (right)

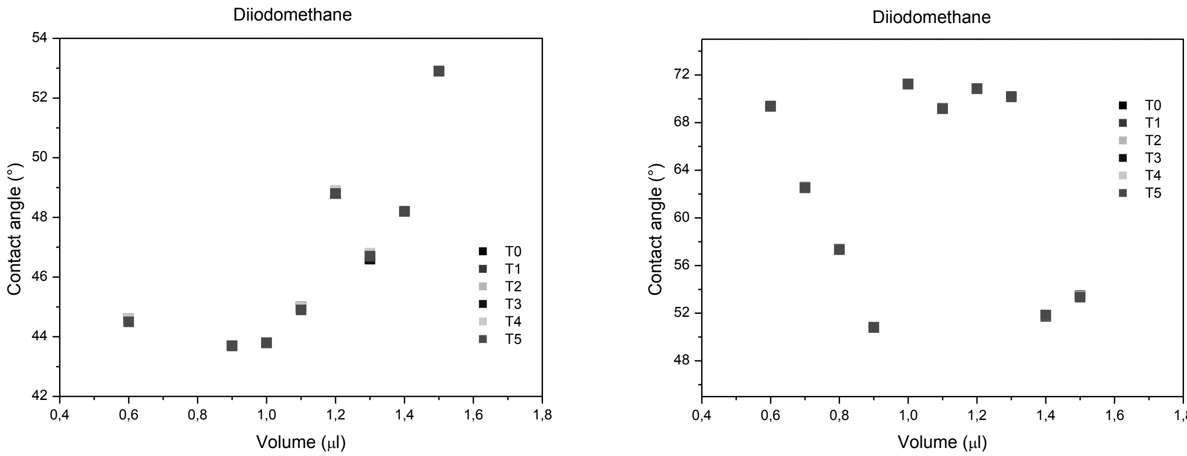

Fig. 6. Contact angle value depending on drop volume of diiodomethane on printing areas (left) and nonprinting areas (right)

In Fig. 6 one can see the values of contact angle of diiodomethane on printing plate. Values of contact angle are lower on the printing areas of the printing plate which is the consequence of chemical structure of surface and liquid (Tab. 1). Increasing drop volume causes significant increase of the contact angle value when measuring on the printing areas (Fig. 6 left).

It can be seen in Fig. 6. right that drop volume of diiodomethane does not have the same impact on contact angle value on nonprinting areas as it has on the printing areas. The results show that, opposite to the printing areas, contact angle decreases values with increase of the drop volume, but in the middle of investigated volume

range is nearly the same as it was at first investigated value. Further increase of the drop volume causes significant decrease of the contact angle value.
Such behaviour of the contact angle on the nonprinting areas of the printing plate could be the consequence of the printing plates surface topolography and chemical structure of the aluminium-oxide (Risovic et al., 2009).

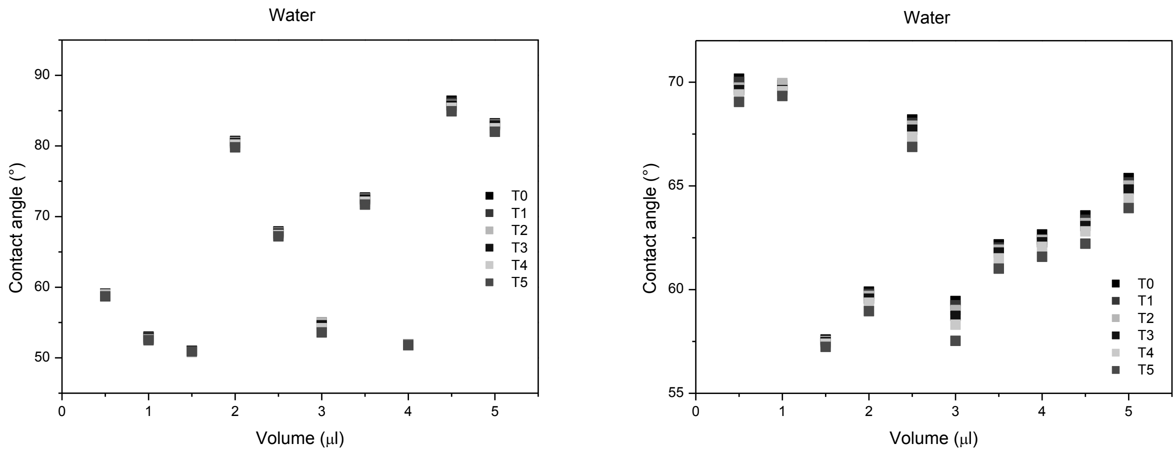

Fig. 7. Contact angle value depending on drop volume of water on printing areas (left) and nonprinting areas (right)

Results of contact angle measurement of water can be seen in Fig. 7. The contact angle of water is relatively high on printing and nonprinting areas. This fact comes as a surprise knowing that nonprinting areas are built from aluminium-oxide which has polar characteristics and should adsorb water very well. This could be explained by “air trap“. As said before aluminium-oxide layer is porous and rough and air could be held in valleys of the investigated surface. This then disables contact between investigated liquid and material and cause higher contact angle values than expected.
Observing the results in Fig. 7 one can see that contact angle value on printing and nonprinting areas changes significantly by change of the drop volume, increasing the drop volume causes increase of the contact angel value. The exceptions from this behaviour are first two volumes on nonprinting areas but as said before this is probably due to the “air trap”.

5. Conclusion

In this paper, the wetting characteristics of printing and non-printing areas of the offset printing plates were defined by measuring the spreading contact angle of standardized liquids changing the drop volume. Results have shown that contact angle values and values of surface free energy of non-printing areas (polar characteristics) have been significantly changed during the time period of measurement (slightly less than 30%). On the other hand surface free energy of printing areas has not significantly changed during the time. Beside time dependant contact angle, volume of the drop proved to be also very important factor in determination of contact angle value, consequently values of the surface free energy.By the nonprinting areas is change of the contact angle value higher when performing measurement in various times than when changing drop volume. On the other hand, drop volume has greater influence on the contact angle values when performing measurement on the printing areas.

One can conclude that dynamic contact angle can give more complex information about the printing plate surface than static one, while it gives information about adsorption velocity which could be essential in printing plate's exploitation, during printing process. This research has also proved that determination of surface properties of a printing plate is complex and could not be done by applying only one measuring method therefore in future when investigating printing plate surface one needs to apply more research methods. Furthermore, measurement of the contact angle proved to be influenced by many parameters which makes it hard to standardize.Therefore, further research has to be directed to the studies related to polar (non-printing) surfaces on the printing plates, which are obviously, because of their porous and rough characteristics, highly sensitive in liquid-solid interfaces but in the same time highly important in achieving high quality printing.

It is highly important to standardize this method for determination of surface properties because in graphic reproduction process, where functional properties of printing plates, and consequently quality level of final graphic product, depend on the wetting properties of surface structures.

6. References

Dimogerontakis, Th.; Van Gils, S.; Ottevaere, H.; Thienpont H. & Terryn, H. (2006).Quantitative topography characterisation of surfaces with asymetric roughness induced by AC-graining on aluminium, *Surf. Coat. Technol.* 201, 918-926

Dörfler, H.-D. (2002) *Grenzflächen und kolloid-disperse Systeme - Physik und Chemie*, Springer-Verlag, ISBN 3-540-42547-0, Berlin

Hamraoui, A., Thuresson, K.; Nylander, T. & Yaminsky, V. (2000). Can a Dynamic Contact Angle Be Understood in Terms of a Friction Coefficient? *Journal of Colloid and Interface Science* 226, 199–204

Lander, L. M.; Siewierski, L. M.; Brittain, W. J. & Vogler, E.A. (1993). A Systematic Comparison of Contact Angle Methods. *Langmuir*, 9, 2237-2239

van Oss, C. J.; Giese, R. F.; Li, Z.; Murphy, K.; Norris, J.; Chaudhury, M. K. & Good, R. J. (1993) *Contact Angle, Wettability and Adhesion*, K. L. Mittal (Ed.), VSP, Utrecht, The Netherlands

de Ruijter, M.; Kolsch, P.; Vouea, M.; de Coninck, J. & Rabe J.P. (1998).Effect of temperature on the dynamic contact angle *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 144, 235–243

Risović, D.; Mahović Poljaček, S.; Gojo, M.(2009). On correlation between fractal dimension and profilometric parameters in characterization of surface topographies. *Applied Surface Science* 255, 4283-4288

Shriver, D. F. & Atkins, P. W. (1999). *Inorganic Chemistry*, 3rd Edition, W. H. Freeman and Company, N