

## The Properties of Water Born Thermoplastic Adhesive for Hot Stamping Multilayer Films

Pranas NARMONTAS<sup>1,2</sup>, Eglė FATARAITE<sup>1,2\*</sup>,  
Virginija JANKAUSKAITE<sup>2</sup>, Asta GUOBIENE<sup>1,3</sup>

<sup>1</sup>*Institute of Physical Electronics, Savanorių 127, LT-50131 Kaunas, Lithuania*

<sup>2</sup>*Research Laboratory of Polymer Products, Faculty of Design and Technologies, Kaunas University of Technology, Studentų 56, LT-50131 Kaunas, Lithuania*

<sup>3</sup>*Department of Physics, Kaunas University of Technology, Studentų 50, LT-50131 Kaunas, Lithuania*

*Received 30 August 2004; accepted 27 October 2004*

The possibility to use water-born adhesive based on the copolymer of vinyl ester of synthetic saturated monocarboxylic acid, methylmethacrylate and 2-ethylhexylacrylate (Veova-10/MMA/2-EHA) modified with titanium dioxide, for the multilayer structures of hot stamping has been investigated. It is shown that for the unfilled adhesive compositions dilatant behaviour under shear flow condition is characteristic. The filling changes viscosity of dispersion and enables to facilitate technological adhesive layer coating procedures.

The evaluation of adhesion properties by indirect method indicates changes of failure mode when adhesive layer thickness increases. The increase of unfilled adhesive layer thickness increases stamps covering irregularities and decreases its boundary zone quality. The optimal layer thickness was found to be 2 µm. The obtained results confirmed the effect of disperse filling as a way to change adhesion and mechanical properties of multilayer structure. The effective amount of disperse filler allows to obtain stamps which bonding quality are close to those of standard. Besides, the increase of filler content in adhesive composition results on the formed stamps hardness changes. The measurements of modulus and break parameters show non monotonous influence of filler content.

*Keywords:* copolymer, adhesion, composition, filling, hot stamping, uniaxial tension

### INTRODUCTION

At present high quality technique, such as photocopiers and imagines scanners, creates possibilities of a counterfeit hazard of documents. To avoid forgeries optical security devices can be used, among which fluorescence paints, thin film layers with embossed holograms can be applied [1].

Irrespective of the intended use or function of hot stamped thin protective films the properties, structure, integrity, functional characteristics, and performance among other things depend on the adhesion between the thin film and the substrate [2]. One of the main factors, is the nature and sizing of adhesive layer, which is used to transport the film to the substrate surface such as paper, plastic, metal, glass, etc. [3–6, 13]. In this case the various compositions of adhesive and methods of their setting can be used. The most popular are solvent born systems used for pressure sensitive or thermoplastic adhesive layer formation [7].

Nowadays more environmentally friendly technology using water born adhesives compositions can be selected. It is important to understand the main factors, which influence the both composition and adhesion properties, i.e. hot stamping quality. There, the creation of water born products with improved properties, and making these products available to replace volatile adhesives are the main goal of investigations [8, 9].

For these purposes water-born adhesives which film forming component are based on the various kinds of Veova (Vinyl ester of Versatic acid) copolymers can be used. More recently, Veova monomers have been studied as co-monomers with (meth)acrylate, which are formulated into paints for more demanding applications such as wood coatings or water based anti-corrosion primers [10]. On the other hand, combination of three monomers such as Veova, soft acrylic monomer 2-ethylhexyl acrylate (2-EHA) or butylacrylate (BA) and the hard methacrylic monomer methyl methacrylate (MMA) can produce more desirable effects in adhesive, structural properties changes and increase field of this composition application [10].

The aim of this research was to investigate water born Veova-10/MMA/2-EHA copolymer dispersion for thermoplastic adhesive layer formation in multilayer films hot stamping and to determine optimal composition structural parameters.

### EXPERIMENTAL

The water-born adhesive to be used was based on the copolymer of vinyl ester of a synthetic saturated monocarboxylic acid  $\text{CH}_2=\text{CHOCOCR}_1\text{R}_2\text{R}_3$ , containing 10 carbon atoms (Veova-10). For investigations the copolymer obtained by emulsion polymerisation of Veova-10/MMA/2-EHA (producer Joint Stock Company "Achema", Lithuania) was used. Solid content of adhesive composition in water medium was of 40 %. Titanium dioxide ( $\text{TiO}_2$ ) was added as a filler. The average particle radius  $r$  of  $\text{TiO}_2$  was 0.34 µm.

\*Corresponding author. Tel.: +370-37-300207; fax.: +370-37-353989.  
E-mail address: [Egle.Fataraitė@ktu.lt](mailto:Egle.Fataraitė@ktu.lt) (E. Fataraitė)

Homogenisation of disperse filled composition was performed at high rotational speed ( $\omega = 50 \text{ s}^{-1}$ ) for 10 min.

Adhesive layer was formed on the multilayer hot stamping foil for paper, produced by Holo 3D S.r.l., (Italy). The total thickness of foil, which consists of aluminum layer, polymer layer for holographic microstructure embossing, release coating and carrier was  $19 \mu\text{m}$ .

Paper *Kymlux* was used as a substrate for holographic foil stamping. Its smoothness according to Bekk and grammage was  $650 \text{ s}$  and  $90 \text{ g/m}^2$ , respectively.

The rheology of solutions under shear flow condition was determined according to Brookfield test method with the rheometer Rheomat RM 180 according to the requirements of standard ISO 2555.

Anilox rolls were used to transport adhesive on the aluminum layer of holographic foil. Engravings on the rolls surface were used to transport a precisely determined quantity of adhesive. Amount of transferred composition was changed by variation of the engraving volume. As a result the adhesive layer of  $1 \div 4 \mu\text{m}$  thickness was formed.

The heated circle shaped metal stamp with diameter of  $16 \pm 2 \text{ mm}$  was used for hot stamping of holographic foil on the paper surface at pressure of  $0.25 \text{ MPa}$  for  $0.3 \text{ s}$ . Adhesion properties of water based adhesive composition were evaluated by the indirect method. This method includes comparison of the stamp covering area and its boundary zone to the standard one. Standard stamp was assumed as stamp, fully transferred on the paper surface with regular, even boundary zone. The procedure of stamp observation consists of three steps: 1) registration of the stamp on the paper surface; 2) registration of the grey level mean value of the obtained digital images (area of testing zone was  $20 \text{ mm} \times 20 \text{ mm}$ ) with CCD camera; 3) qualitative evaluation of the adhesion properties, which were assumed as a ratio:

$$A = (GL - GL_{st}) / GL_{st}, \quad (1)$$

where  $GL$  and  $GL_{st}$  are grey levels of obtained and standard images, respectively.

The grey level measurements were performed on the standard image processing system. For each experimental point at least 10 stamps were tested.

Atomic force microscope (AFM) NANOTOP-206 with a silicon cantilever was used in the contact mode for the observation of the formed adhesive layer surface topography with  $10 \mu\text{m} \times 10 \mu\text{m}$  field-of-view.

The constant load scratch tests were performed in order to investigate the changes of hot stamped films mechanical properties [12]. Test was carried out under controlled conditions with a device that consisted of a loaded probe with a diamond indenter moving linearly along the sample with a constant speed of  $10 \text{ mm/min}$  and  $10 \text{ mm}$  scratch length. The compressive load from  $0.1 \text{ N}$  up to  $1.5 \text{ N}$  was applied to indenter to perform cracks on the surface of stamp.

The breakdown of the stamps was evaluated by the topography measurements across obtained scratches using computer-based profilometer.

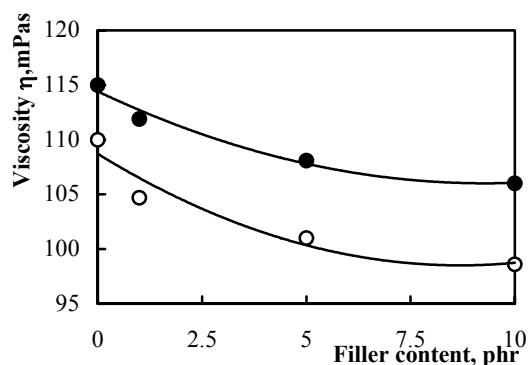
Mechanical properties of multilayer holographic foil were evaluated during uniaxial tension test performed on

the universal testing machine FP10/1 at reversal speed rate  $100 \text{ mm/min}$ . The working area of dumbbell shaped specimens was  $3 \text{ mm} \times 1 \text{ mm}$  and thickness varied from  $20 \mu\text{m}$  up to  $24 \mu\text{m}$ .

## RESULTS AND DISCUSSIONS

It is known that the behaviour of water-born dispersion during coating depends not only on the volume of engravings on the surface of anilox rolls, but on the rheological properties of the adhesive, also. Deviation from the Newtonian response causes problems in the coating operations [11, 7]. The experimental plots presented in the Fig. 1 indicate that at isothermal testing conditions the increase of shear rate from  $42 \text{ s}^{-1}$  up to  $50 \text{ s}^{-1}$  results on the increase of VeoVa-10/MMA/2-EHA copolymer dispersion viscosity. That tends to the conclusion about dilatant behaviour of composition, which can be caused due to orientation and alignment of dispersion particles [11]. On the other hand, these changes can be related to the increase of intermolecular interaction of copolymer constituents. As a result of such non-Newtonian behaviour during the deposition of a smooth and uniform adhesive layer on the holographic foil void spots appear in places on the web.

Disperse filling with  $\text{TiO}_2$  particles can be considered as a possible way to eliminate this disadvantage, i.e. to achieve thickening of dispersion. The titanium dioxide modified composition behaviour under shear shows the decrease of dispersion viscosity when the filler content in the dispersion increases. In this case more visible viscosity changes for compositions filled up to 5 phr of  $\text{TiO}_2$  appear. As one can see, filled with 5 phr of  $\text{TiO}_2$  composition at shear rate of  $50 \text{ s}^{-1}$  shows the same viscosity values as those of unfilled at shear rate of  $42 \text{ s}^{-1}$ .



**Fig. 1.** The influence of filler content on viscosity  $\eta$  of VeoVa-10/MMA/2-EHA at different shear rate  $\dot{\gamma}$ ,  $\text{s}^{-1}$ :  $\circ$  – 42,  $\bullet$  – 50

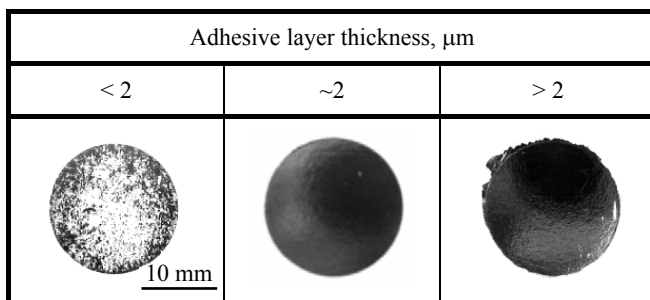
The ability to use water born composition as thermoplastic adhesive layer during hot stamping procedure was evaluated according to the results of adhesive properties changes determined by indirect method and by scratch test results.

The first method was based on the comparative evaluation of the stamps covered area and boundary zone irregularities to the standard one. Three typical kinds of obtained stamps in dependence on adhesive layer thickness were found. Their characteristic pictures are presented in

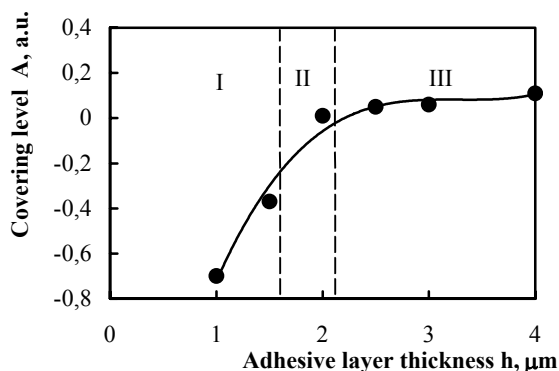
the Table 1. One can see that increase of adhesive layer thickness results on the increase of covering area of stamps, but on the other hand the increase of boundary zone irregularities is observed. The results of comparative analysis of obtained stamps in dependence formed on adhesive layer thickness are presented in Fig. 2. In this evaluation negative values of parameter  $A$  characterize stamps, which covering area is lower than that of standard, for which  $A=0$ , and positive  $A$  values indicate that covering area of stamp is higher than those of standard.

The holographic foil with adhesive layer, which thickness is lower than  $2 \mu\text{m}$ , was not fully transferred to the surface of the paper. The obtained negative  $A$  values leads to the conclusion that the formed adhesive layer, which thickness is lower than  $2 \mu\text{m}$ , shows low adhesion of multilayer holographic structure to the paper substrate.

**Table 1.** The typical view of stamps upon adhesive layer thickness



The results show also, that at the selected hot stamping conditions not only delaminating of the carrier layer through release wax coat of multilayer structure takes place, but cohesively failure through the all other layers such as aluminium, polymer with embossed holographic microstructure and the adhesive layer is observed. Otherwise, at higher than  $2 \mu\text{m}$  adhesive layer thickness, the parameter  $A$  values become positive. The  $A$  values practically do not change, when the adhesive layer thickness increases. The covering area of stamps is obtained without interruptions, but the boundary line is irregular and uneven (see Table 1). It is believable, that it is due to plastic state of the adhesive layer in the nearest zone of stamp during hot stamping procedure, but adhesion strength in these regions can not be achieved due to absence of additional required pressure [13].



**Fig. 2.** The covering quality of hot stamped holographic foil vs adhesive layer thickness

The approximation of obtained results by a least square method showed that dependence between the parameter  $A$  and adhesive layer thickness  $h$  can be expressed by the third order polynomial relation ( $R^2 = 0.98$ ):

$$A = 0.0684h^3 - 0.673h^2 + 2.2046h - 2.3222 \quad (2)$$

The variation of results confirms suggestion that bonding quality can be varied by changing thickness of the adhesive layer. Otherwise, the use of selected composition for adhesive layer formation does not lead to obtain stamps which covering was like those of standard.

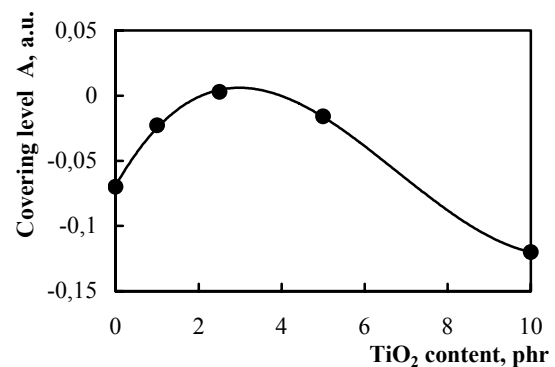
As one of the simplest ways to modify adhesion properties of composition is disperse filling. So, compositions, containing various contents  $\varphi$  of  $\text{TiO}_2$  were investigated. Multilayer structures with adhesive layer of  $2 \mu\text{m}$  of thickness, providing the best covering results were used. Fig. 3 shows covering quality of holographic stamps obtained after hot stamping of holographic foil using thermoplastic adhesive layer containing 0–10 phr of titanium dioxide.

The effect of filling on the hot stamping quality has non-monotonous character. The increase of parameter  $A$  when filler content increases up to 2.5 phr and decrease at higher filler content was found. It was determined also, that use of the composition with 2.5 phr of  $\text{TiO}_2$  allows to obtain stamps, with covering quality similar to that of standard ( $A = 0$ ).

As in the above discussed case (see Eq. 2), relation between the adhesive composition and adhesion properties of the multilayer structure can be also approximated by the third order polynomial relation ( $R^2 = 0.99$ ):

$$A = 0.0006 \varphi^3 - 0.012 \varphi^2 + 0.0557 \varphi - 0.0692 \quad (3)$$

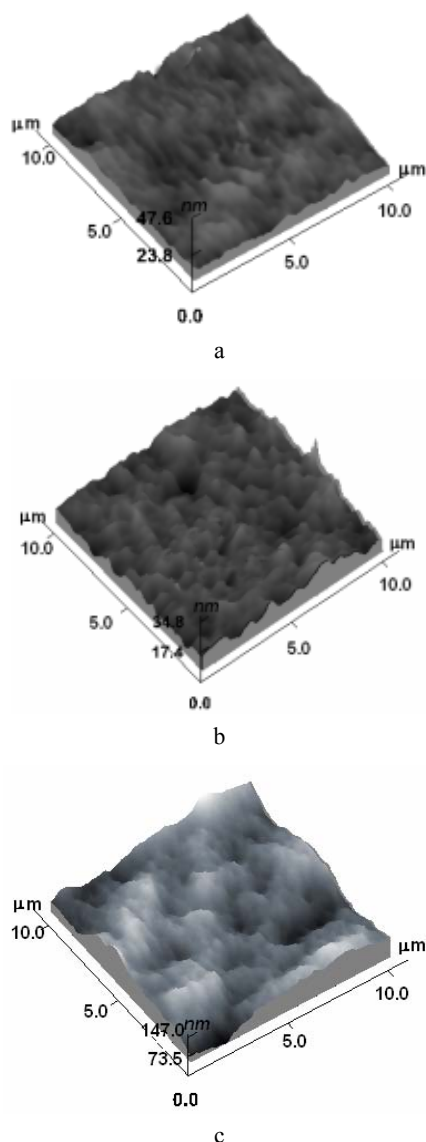
Meanwhile, values of the coefficients are significantly lower than those obtained above. This indicates significance and importance of the adhesive layer thickness on the hot stamping quality.



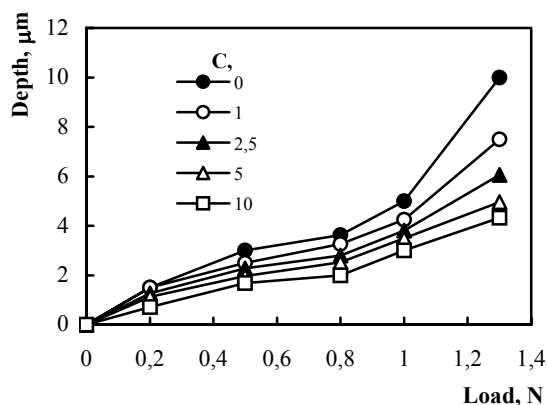
**Fig. 3.** The covering quality of holographic stamps vs filler content in adhesive composition

Properties changes after adhesive layer modification by filling can be explained by changes in surface microstructure. AFM investigations of the adhesive layer surface topography shows increase of surface roughness when filler content in the composition increases (Fig. 4). For unfilled adhesive layer composition “uniform” smooth pattern of surface roughness over the entire area is characteristic (Fig. 4, a). In that time filled compositions show domains with the expressed shape (Fig. 4, b and c), with increase of roughness with the growth of filler

content. It is believable that high density of created domains at 2.5 phr of  $\text{TiO}_2$  is one of the main reasons



**Fig. 4.** AFM images of VeoVa-10/MMA/2-EHA adhesive surface topography filled with different content of  $\text{TiO}_2$ : a – 0, b – 2.5 phr, c – 10 phr



**Fig. 5.** The influence of scratch load on the groove depth for adhesive compositions modified with various amounts of  $\text{TiO}_2$

resulting on the both adhesion and cohesion properties changes of over all multilayer structure. It also influences the more clear disconnection through release coating of the hot-stamped multilayer holographic foil on the paper surface.

In order to evaluate influence of adhesion composition changes on the overall stamp mechanical properties scratch test was performed. In Fig. 5 presented results indicate that increase of filler content results on the decrease of scratched groove depth. It is related to the increase of holographic film hardness. Besides, the increase of scratch load results on the increase of composition sensitivity to the applied load.

For example, the addition of 1 phr and 2.5 phr of  $\text{TiO}_2$  decreases depth of scratched groove 30 % and 50 %, respectively, at 1.2 N of applied load. In the case of lowest load only negligible changes of groove depth was found. The decrease of groove depth with growth of the filler content in the adhesive indicates also on the wear resistance of the formed structure on the paper surface [16]. The data of tensile tests of freestanding films in dependence on the adhesion composition formed on the film surface are presented in Table 2.

**Table 2.** Mechanical properties of multilayer holographic films

Parameter	$\text{TiO}_2$ content, phr				
	0	2.5	5	7.5	10
Tensile strength, MPa	90.33	87.71	88.55	106.3	98.02
Elongation at break, %	67	66	44	88	76
Young's modulus, MPa	771	768	882	938	817

The elasticity modulus and break parameters values indicate the non-monotonous influence of the filler content. As a rule, the multilayer structures comprising adhesive layer with 2.5 phr of  $\text{TiO}_2$  shows insignificant degradation of over all mechanical properties during tension. While at higher than 5 phr filler content, tendency to mechanical properties improvement, as compared with pure adhesive, was observed. These data show the influence of adhesive layer properties on the all multilayer structure properties and indicate increase of structure defectiveness when adhesive consists of 2.5 phr of  $\text{TiO}_2$ . From the practical point of view, such defective structure allows to obtain high quality stamps during hot stamping.

## CONCLUSIONS

It was shown that water-born VeoVa-10/MMA/2-EHA copolymer dispersion could be used for adhesive layer formation. The hot stamping quality highly depends on the holographic foil surface formed adhesive layer thickness and composition.

The dilatance under shear flow condition can be decreased by disperse filling of composition with titanium dioxide particles.

The evaluation influence of adhesive layer thickness on the hot stamping quality showed that the increase of adhesive layer thickness increases stamps covering

irregularities and decreases its quality. The effective amounts of disperse filler allows to obtain stamps which covering level is like those of standard.

Disperse filling is a possible way to increase mechanical properties of multilayer structure and increase its wear resistance.

### Acknowledgments

The work was supported by Lithuanian Science and Studies Foundation.

### REFERENCES

1. **Van Renesse, R. L.** Optical Documents Security, TNO Institute of Applied Physics, 1998.
2. **Cheremisinoff, N. P.** (Ed.) Handbook of Engineering Polymeric Materials. Marcel Dekker, New York, 1997: 881 p.
3. Optical Document Security. Document Protection by Holograms. Ed. by Colgate, G., Jr. Boston, Artech House, 1998.
4. **Fotea, C., D'Silva, C.** The Use of Silane Reagents as Primers to Enhance the Adhesion of Chromium Tanned Heavy-Duty Leather (Salz leather) *International Journal of Adhesion & Adhesives* 24 2004: pp. 1 – 7.
5. **Serrano, E.** A Numerical Study of the Shear-Strength-Predicting Capabilities of Test Specimens for Wood-Adhesive Bonds *International Journal of Adhesion & Adhesives* 24 2004: pp. 23 – 35
6. **Roberta, C., Crespy, A., Bastide, S., Lopez-Cuesta, J.-M., Kerboeuf, S., Artigue, C., Grard E.** Adhesive Properties of Silicone Polymers on Some Typical Opto-Electronic Substrates: Influence of the Network Density *International Journal of Adhesion & Adhesives* 24 2004: pp. 55 – 68.
7. Handbook of Pressure Sensitive Adhesive Technology. Ed. by. D. Satas, Van Nostrand Reinhold Company Inc., 1982: 620 p.
8. **Grisby, W. J., Ferguson, Ch. J., Franich, R. A., Russell, G. T.** Evaluation of Latex Adhesives Containing Hydrophobic Cores and Poly(vinyl acetate) Shells: Potential to Improve Poly(vinyl acetate) Performance *International Journal of Adhesion & Adhesives* 2004 (articles in press).
9. **Baransten, H., Gubbels-van Hal, W. M. L. G.** Environmental Risk Assesmenmt of VeoVa-10, NOTOX project, Final Report, 2003: 19 p.
10. One-Component Chlorine-Free Waterborne Primers for Untreated Polypropylene, Tech. paper SC:3007-01. Resolution Performance Products LLC Research Technical Center Louvain-la-Neuve, Belgium.
11. **Macosko, Ch. W.** Rheology, Principles, Measurements and Applications. VCH Publishers, Inc, 1994.
12. Overvies of Mechanical Testing Standards. Applications Bulletin. CSM Instruments. Advances Mechanical Surface Testing. No.18. September, 2002.
13. **Pocius, A. V.** Adhesion and Adhesives Technology. Munchen, Hanser, 2002: 219 p.
14. **Jardnet, V., Morel, P.** Viscoelastic Effects on the Scratch Resistance of Polymers: Relation Between Mechanical Properties and Scratch Properties at Various Temperatures. *Progress in Organic Coatings* doi: 10/1016/porgcoat. 2003.02 002
15. **Jardnet, V., Zahouani, Loubet, J. L., Mathia, T. G.** Understanding and Quantification of Elastic and Plastic Deformation During a Scratch Test *Wear* 218 1998: pp. 8 – 14.
16. **Xie, Y., Hawthorne, H. M.** On the Possibility of Evaluating the Resistance of Materials to Wear by Ploughing Using a Scratch Method *Wear* 240 2000: pp. 65 –71.

DOI: 10.5755/j02.ms.26651