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OPEN

Arch. Min. Sci., Vol. 59 (2014), No 1, p. 169–178

Electronic version (in color) of this paper is available: http://mining.archives.pl

DOI 10.2478/amsc-2014-0012

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WATERPROOF ANTI-EXPLOSIVE POWDERS FOR COAL MINES

WODOODPORNE PRZECIWWYBUCHOWE PYŁY DLA KOPALŃ WĘGLA

Limestone powder characterized by hydrophobic properties is used as an anti-explosive agent in coal mining industry. Unfortunately, the standard method of producing such powder by milling limestone with stearic acid is practically unprofitable in many modernized quarries and plants, and sometimes literally impossible due to the introduction of technological changes and implementation of modern mills. Then new methods of hydrophobization of limestone surfaces ought be searched. In the work two methods hydrophobization: from the stearic acid vapour phase and from silicone solutions are proposed.

Lime dust from the Czatkowice Quarry of Lime was used as a raw material during investigations. It is a good agent for research because it is possible to compare the properties of samples modified in this work to the properties of anti-explosive lime powder (Polish Standard, 1994) used in mining industry in Poland.

The first technique of limestone powder hydrophobization was carried out in an apparatus of own design (Vogt, 2008, 2011), and it consisted in free sedimentation of the powder layer dispersed by stearic acid vapour in powder counter current flow. The second way of modification consisted in mixing in the evaporating dish substrates: limestone powder and dope – silicone solution – Sarsil® H-15 (Vogt & Opaliński, 2009; Vogt & Hołownia, 2010). Evaluation of properties so-obtained waterproof powders was carried out according to the Polish Standard, as well as using original powder determination ways, with the Powder Characteristic Tester (Index tables, Tablets & Capsules, 2005). Moreover water vapour adsorption isotherms were obtained and the thermal decomposition of powder was made. All modified samples acquired the hydrophobic character. Therefore we can state that the both proposed methods of hydrophobization of the limestone powder are useful. The parameters obtained with the use of Powder Characteristics Tester enable us to make a characterization of limestone properties not only as a water resistant material but also from the cohesion point of view. On the base of TG, DTG or DTA and EGA curves for all investigated materials was stated that the character of the thermal decomposition of modified samples is the same as this one for raw powder, what is profitable for application of hydrophobized powders as an anti-explosive agent.

Keywords: limestone powder, hydrophobization, flow properties, adsorption, thermal decomposition

W górnictwie węgla kamiennego używany jest hydrofobowy pył wapienny jako substancja stosowana w systemie zabezpieczeń przeciwwybuchowych (Cybulski, 2004). Niestety, dotychczasowy sposób wy-

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twarzania takiego produktu polegający na współmieleniu kamienia wapiennego z kwasem stearynowym staje się praktycznie niemożliwy do stosowania w nowoczesnych zakładach np. kamieniołomy. Sytuacja taka jest wynikiem wprowadzania zmian technologicznych, głównie związanych z wymianą starych konstrukcji młynów na nowe urządzenia.

Tym samym istnieje potrzeba poszukiwania nowych metod hydrofobizacji powierzchni pyłów wapiennych. W pracy omówiono dwie nowe metody hydrofobizacji pyłu wapiennego: za pomocą par kwasu stearynowego oraz roztworu silikonowego – Sarsil® H-15. Podczas badań używano surowego pyłu wapiennego pochodzącego z Kopalni Kamienia Wapiennego w Czatkowicach. Materiał ten jest dobrym materiałem do badań gdyż istnieje możliwość porównywania właściwości materiałów hydrofobowych otrzymanych w pracy z właściwościami handlowego pyłu przeciwwybuchowego (Polska Norma, 1994), używanego w polskich kopalniach.

Pierwszy sposób hydrofobizacji pyłu wapiennego, polegający na swobodnym opadaniu pyłu wapiennego w oparach kwasu stearynowego przepływających w przeciwprądzie, przeprowadzono w aparacie własnej konstrukcji (Vogt, 2008, 2011). Aparat gwarantuje dobry kontakt modyfikatora z ziarnami pyłu. Pył opadając, nie napotyka żadnych przeszkód ulegał rozproszeniu, a wprowadzony w stanie parowym kwas stearynowy może swobodnie osiadać na jego powierzchni zewnętrznej oraz penetrować w głąb porów, blokując je dla wilgoci. Drugi sposób hydrofobizacji sprowadzał się w uproszczeniu do zmieszania substratów: pyłu wapiennego i domieszki silikonowej – Sarsil® H-15, w parownicy (Vogt i Opaliński, 2009; Vogt i Hołownia, 2010). We wstępnych badaniach określono objętość preparatu, jaką trzeba dodać do pyłu w celu uzyskania optymalnych warunków kontaktu preparatu z ciałem stałym. Otrzymany po modyfikacji materiał był zbrylony w niewielkim stopniu, a jego całkowite rozdrobnienie uzyskano poprzez przecieranie pyłu przez sito o odpowiednim wymiarze oczek.

Badanie właściwości tak otrzymanych hydrofobowych materiałów przeprowadzono w oparciu o PN (Polska Norma, 1994), jak również w oparciu o standardowe metody badania materiałów proszkowych z użyciem aparatu Powder Characteristic Tester (Index tables, Tablets & Capsules, 2005) (Tablica 2,3). Oceny stopnia hydrofobizacji materiałów po modyfikacji dokonano, w przypadku proszku hydrofobizowanego parami kwasu stearynowego, w oparciu o procedurę opisaną w Polskiej Normie (1994), oznaczając procentową zawartość kwasu stearynowego. Otrzymany podczas badań pył hydrofobizowany kwasem stearynowym zawierał 0,18% modyfikatora, co jest ilością dopuszczalną przez Polską Normę (1994).W celu oceny właściwości hydrofobowych materiału modyfikowanego roztworem silikonowym do badań zaadaptowano technikę pomiaru zwilżalności ziaren węglowych „film flotation" (Fuerstenau i Williams, 1987) przyjmując, jako materiał odniesienia hydrofobizowaną mączkę wapienną z Kopalni Kamienia Wapiennego w Małogoszczy. Opracowano metodę wyznaczania współczynnika C określonego, jako stopień hydrofobizacji (Vogt i Opaliński, 2009). Średnia wartość C = 84% wskazuje, że materiał modyfikowany preparatem silikonowym uzyskał odpowiednie właściwości hydrofobowe. Tym samym oba materiały po modyfikacji uzyskały zadowalające właściwości wodoodporne.

Ponadto, dla badanych pyłów wyznaczono izotermy adsorpcji pary wodnej (Rys. 1). Uzyskane niższe wartości adsorpcji dla materiałów po modyfikacji niż dla proszku surowego potwierdzają, że materiały posiadają charakter hydrofobowy, co pozwala stwierdzić, że obie proponowane metody hydrofobizacji są użyteczne do produkcji wodoodpornego pyłu wapiennego.

Analizę termiczną pyłów wapiennych wykonano w celu porównania efektu cieplnego przemian zachodzących podczas ogrzewania pyłów modyfikowanych z efektem cieplnym zachodzącym podczas ogrzewania surowego pyłu wapiennego. W trakcie badań użyto termowagę firmy TA Instruments 2960 SDT ze sprzężonym spektrometrem masowym firmy Balzers TermoStar 300. Otrzymane wynikiprzedstawiono na Rys. 2. Linie ciągłe na Rys. 2a i 2b przedstawiają przebieg krzywych TG, DTG oraz DTA dla pyłu surowego. Linie przerywane zostały otrzymane dla pyłu modyfikowanego kwasem stearynowym (Rys. 2a) oraz preparatem SARSIL® H-15 (Rys. 2b). Na Rys. 3 zobrazowano wyniki analizy zawartości tlenku węgla IV w składzie gazów otrzymywanych podczas rozkładu termicznego pyłu wapiennego (EGA). Krzywa otrzymana dla pyłu modyfikowanego kwasem stearynowym w zasadzie pokrywa się z krzywą otrzymaną dla pyłu surowego.

Parametry uzyskane z użyciem aparatu Powder Characteristics Tester umożliwiły scharakteryzowanie pyłów wapiennych nie tylko pod kątem ich właściwości hydrofobowych, ale także właściwości kohezyjnych i przepływowych.

Słowa kluczowe: pył wapienny, hydrofobizacja, właściwości przepływowe, adsorpcja, rozkład termiczny

1. Introduction

As a precaution against coal dust explosions, stone powder is spread within mine barriers. During an explosion the stone powder disperses, mixes with the coal dust and prevents flame propagation, acting as an inhibitor. Stone powder reduces the flame temperature to a point where devolatilization of the coal dust can no longer occur; starved of fuel, the explosion is inhibited. The amount of stone powder required to inert an explosion depends on: particle size of the stone material and type of the coal dust, as well as atmosphere composition (humidity, content of air and methane) present in underground coal mines.

Two types of stone powder are produced (regular and water-proof) which are used for sprinkling and for constructing dust barriers (Cybulski, 2004; Vogt & Buczek, 2007; Lebecki & Małachowski, 2012). A regular limestone powder is most commonly used for these purposes. Its major defect is its tendency to lose volatility, because of agglomeration under humid conditions, often reaching 100% water saturation in mine atmospheres. Using the waterproof powder may eliminate it. Such powder has been produced by coating regular powder with stearic acid during grinding in stone mills (Polish Standard, 1994; Lebecki, 1993). In modernized quarries and plants, modern mills of a complex construction are employed, in which contamination with hydrophobizing agents is practically avoided. For this reason, new methods of modifying the character of limestone surfaces are searched for.

2. Experimental

2.1. Materials

In this work limestone powder (meal) from the Czatkowice Lime Quarry (Buczek & Vogt, 2007) with the particle diameter less than 80 μm was used as a raw material during researches. This powder is, among others, used in the coal mining industry as one of the elements of the anti-explosive safety system (Polish Standard, 1994; Lebecki, 1993; Skalski, 2005; Man & Teacoach, 2009).

The average chemical composition of meal in accordance with the manufacturer's data is presented in Table 1. The real density of the meal, marked with the method of helium picnometry with the use of the AccuPyc 1330 apparatus, amounts to 2.7642 g/cm^3.

TABLE 1

Chemical composition of limestone meal – manufacturer's data

Component	$CaCO_3$	SiO_2+NR	$MgCO_3$	Fe_2O_3	Al_2O_3	Na_2O	K_2O	Heavy metals
(% w/w)	96.00	1.50	1.50	0.11	0.08	0.023	0.037	In trace amounts

Industrial modifiers were chosen for research as they guarantee good contacting of powder grains with a hydrophobizing preparation. Stearic acid is used in mining production plants for the production of water-resistant powder preventing the coal dust explosion in mines (Polish Standard, 1994).

Another dope used in the research is an existing on the market representative of groups of compounds applied for the hydrophobization processes of mineral materials; this is a silicone preparation with the marketing name Sarsil® H-15 produced by the Chemical Plant "Polish Silicones" Ltd in Nowa Sarzyna. The solution of methyl salicylate resin in organic solvent – has got the density of 0.78 kg/m^3.

2.2. Manufacturing methods

Two methods to obtaining of hydrophobic material are proposed: hydrophobization from stearic acid vapour and from silicone solutions.

The commercially used in mining industry hydrophobic limestone powder has been produced by coating regular powder with stearic acid during grinding in stone mills. The accurate description of techniques applied for the hydrophobization of limestone powders was discussed in the earlier works by the authors (Vogt, 2008, 2011; Vogt & Opaliński, 2009, Vogt & Hołownia, 2010). During these researches stearic acid vapour is contacted with limestone meal in a counter current flow in an installation of own design (Vogt, 2011). The second method of producing of hydrophobic limestone powder consists in mixing raw powder with commercial silicone solution in the evaporating dish. The initial research determined the liquid dope volume that should be added to the powder in order to obtain optimal conditions for the contact of the preparation with a solid.

3. Investigation of materials properties

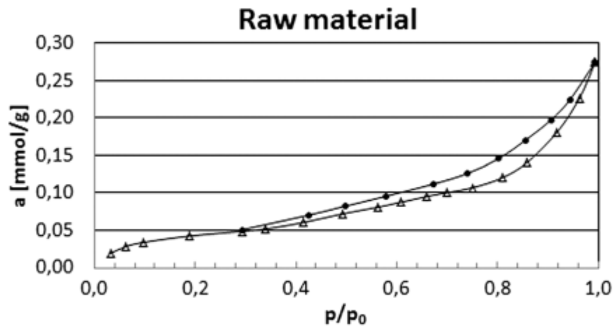
3.1. Evaluation of the hydrophobization degree

Materials obtained in this way, may be used as an anti-explosive agents in mining industry. This waterproof product protects human life so its properties are very important and should be well known. One of the most important issues is the determination of the index of hydrophobization of samples. It is easy to determine it when stearic acid is used as a modifier, because there is a standard, which defines this measurement (Polish Standard, 1994). The manufactured, above written way, sample contains 0.18% of stearic acid, being an acceptable level according to the Polish Standard (Polish Standard, 1994).

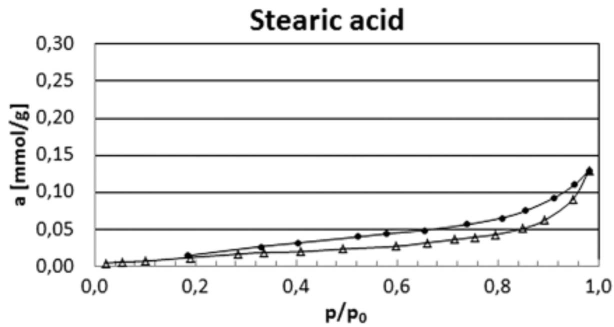
In the case of sample modified with the use of silicone solution authors had to work out the method for determination of hydrophobization C coefficient. The film flotation method (Diao & Feuerstenau, 1991) was used for this purpose when the commercial material produced by coating regular powder with stearic acid during grinding in stone mills was used as a comparative sample (Polish Standard, 1994). The C coefficient defined to what extent the hydrophobic properties of the sample obtained with the use of silicone solution as a modifier are different from the hydrophobic properties of the commercial sample on contact with a suitable (10, 20, and 60% (w/w)) methanol solution. The average value of the C = 84% coefficient shows that the sample doped by silicone solution obtained sufficient hydrophobic properties.

3.2. Water vapour adsorption

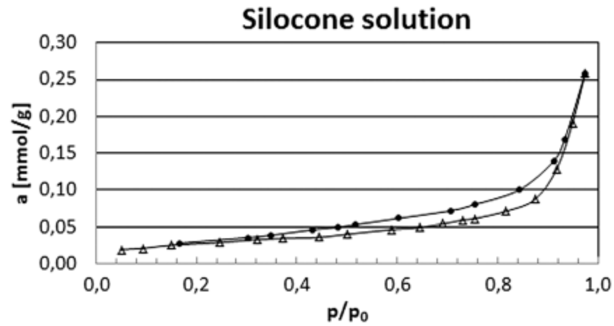
The hydrophobicity of obtained materials has been also studied, by the determination of water vapour adsorption isotherms, using the liquid microburettes (Fig. 1). The lesser water vapour adsorption for the hydrophobized powders (Fig. 1), especially for the sample modified with the use of stearic acid proves that products have achieved the water-resistance.



a)



b)



c)

Fig. 1. Water vapour adsorption isotherm for limestone powder a) raw, b) hydrophobized in stearic acid vapour, c) hydrophobized in silicone solution (Δ – sorption; · – desorption curve)

3.3. Measurement of flow powder properties

Obtained samples were analyzed with the use of the research methods originally applied in the powder technique due to the powder state of the material. It is interesting to know how the modification process influenced the change of typical flow limestone meal properties. These properties are as well as hydrophobicity an important quality when we look at the possibility of using modified powders as an anti-explosive agent in mining industry. During researches Powder Characteristics Tester (PChT) – type PT-E, Ser. No. 90133 was used.

Carr (1965) has tried to evaluate powder's flowability and floodability in a numerical manner with the combination of listed in Table 2 various physical characteristics. The tables for the conversion of the measured figures into a common index were published. In order to make an evaluation of the applied modifiers influence on the flow properties of the analyzed materials, the following densimetric values were determined for raw and modified limestone powders: loose bulk density and packed bulk density or repose angle and fall angle. The compressibility, which is an equivalent of the Carr's index (1965) as well as dispersibility of powders, and the Hausner's ratio (1967) and difference angle, which characterizes materials from the cohesiveness point of view were calculated on the basis of the obtained results (Table 2).

TABLE 2

The characteristic of raw and hydrophobized limestone powders

Characteristics	**Material**		
	Raw	**Modified by stearic acid**	**Modified by silicone solution**
Bulk density (kg/m^3)	724	798	790
Packed bulk density (kg/m^3)	1475	1377	1414
Repose angle (deg)	52	47	37
Fall angle (deg)	35	33	34
Difference angle (deg)	17	14	3
Dispersibility (%)	20	41	16
Carr's ratio (%)	50	42	44
Hausner's ratio	2.0	1.7	1.8

The parameters obtained with the use of PChT enable us to estimate the flowability and volatility of powders and give the possibility of determining the properties of limestone powder from the cohesion point of view. The obtained results may be used to assess the direction of changes of flow properties of limestone powders, which were caused by the hydrophobization process. The obtained results allow the determine flow properties of the analyzed materials in a numerical manner. There are special tables (Index tables, Tablets & Capsules, 2005) available which make it possible for the measured parameters to be assigned appropriate ranges of the flowability and floodability index values. Table 3 presents the compressibility and dispersibility values calculated for raw and modified powders and their corresponding ranges of flowability and floodability index values.

TABLE 3

Values of compressibility and dispersibility calculated for raw and modified powders and their corresponding ranges of flowability and floodability index values

Material	**Modifier**	**Compressibility (C), dispersibility (R) and their corresponding index values**			
		C (%)	**Flowability index**	**R (%)**	**Floodability index**
Meal	Lack	50.9	0-19	20	60-79
Meal	Stearic acid	39.8	0-19	42	80-100
Meal	SARSIL® H-15	44.1	0-19	16	40-59

The modified materials constitute the same group of materials as raw meal, and they may be assigned the same range of the flowability index (Index tables, Tablets & Capsules, 2005). The meal modified with stearic acid is characterized by dispersibility allowing assigning the highest range of floodability index values to these materials (Table 3). The determined dispersibility of the SARSIL® H-15 modified material is generally comparable for raw powder.

3.4. Thermal decomposition

The thermal decomposition of the limestone powders hydrophobized by commercial modifiers was studied. Generally the role of limestone powder in the system of protection against explosions brings to the increasing of content of non-combustible parts in coal dusts and physical prevention of the flame propagation. However, this role is much wider. Under the influence of the flames temperature comes to the thermal decomposition of limestone powder and both calcium oxide and carbon oxide (IV) are emitted. This endothermic process consumes some of the flame energy. The gases mixture is enriching in non-flammable CO_2. It causes the reduction of the system's explosion. So the limestone powder has a bigger efficacy than other anti-explosive agents. By implication, analysis of the thermal decomposition of modified limestone powder may be important when these one is characterized as the anti-explosive agent.

The thermo balance TA Instruments 2960 SDT was used during researches. DTA curves and the composition of obtained gasses (EGA) were measured. The results are showed in the Figure 2, 3. The continuous line (Fig. 2a, 2b) represents the course of TG, DTG and DTA curves for the raw material. The dashed lines were obtained for limestone powder modified by stearic acid (Fig. 2a) and silicone solution (Fig. 2b).

The CO_2 contents in emitted gasses showed in the Figure 3 (EGA). The curves obtained for modified powders overlaps with this one obtained for the raw material.

The little differences between of courses of TG, DTG or DTA curves for all investigated materials were stated. The obtained results show that the character of the thermal decomposition of modified samples is the same as this one for raw powder, what is profitable for application of hydrophobized powders as an anti-explosive agent.

4. Conclusions

Both the sample modified by stearic acid and doped silicone solution acquired the hydrophobic character. The lesser water vapour adsorption for the hydrophobized powders (Fig. 1) especially for sample modified with the use of stearic acid proves that the product has achieved the water-resistance. Therefore we can state that the both proposed methods of hydrophobization of the limestone powder are useful.

It was interesting how the modification process influenced the change of typical limestone powder properties. The parameters obtained with the use of Powder Characteristics Tester enable us to make a characterization of limestone properties not only as a water resistant material bat also from the cohesion point of view. It may be assumed that in the case of modified powders (of lower compressibility) flow disturbances will be present on a smaller scale than in the case of a raw material. Taking into account the fact that generally the limestone meal modified with

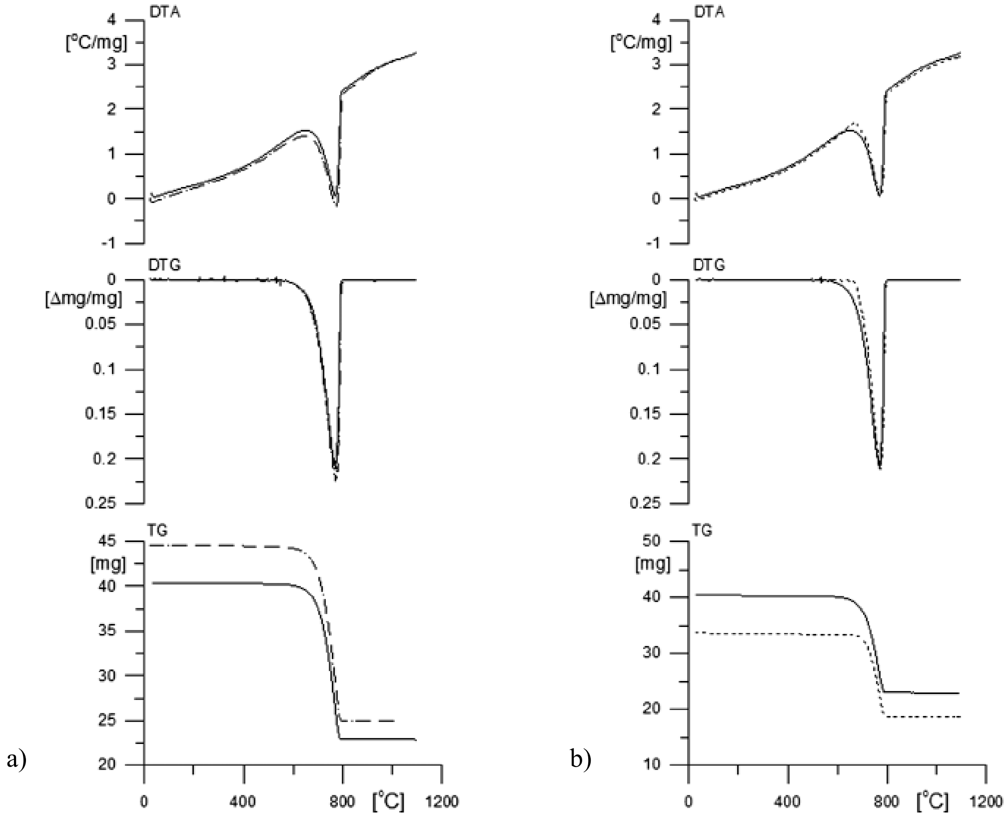


Fig. 2. TG, DTG and DTA curves for limestone powder: raw – continuous line, a) modified by stearic acid – dashed line, b) modified by silicone solution – dashed line

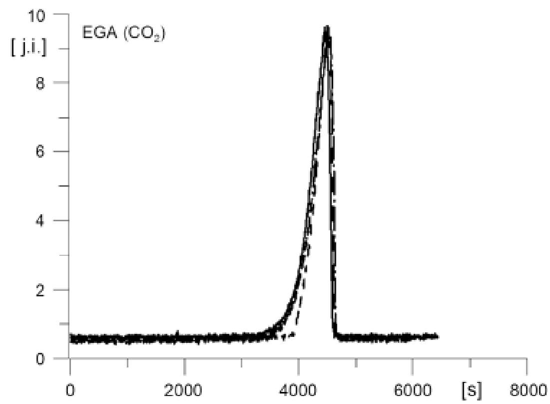


Fig. 3. EGA curves for limestone powder: raw –continuous line modified by stearic acid or modified by silicone solution – dashed line

stearic acid achieved a considerable increase in the dispersibility value in relation to the raw material; it should be assumed that precisely this modifier is the best for improving floodability of limestone powder.

On the base of TG, DTG or DTA and EGA curves for all investigated materials was stated that the character of the thermal decomposition of modified samples is the same as this one for raw powder, what is profitable for application of hydrophobized powders as an anti-explosive agent.

Acknowledgements

The authors are grateful to the AGH University of Science & Technology (Project No. 11.11.210.244) for financial support of this work.

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Received: 16 April 2013