PROGRESS IN COLOR, COLORANTS AND COATINGS

available online @ www.pccc.icrc.ac.ir

Prog. Color Colorants Coat. 13 (2020), 167-175

Ministry of Science, Research and Technology
Institute for Color Science and Technology

Identification and Evaluation of Replaced Materials of Titanium Dioxide Pigment in Alkyd Resins and Investigation of their Properties

F. Tahmasb Pour Afshar, N. Ramezanian*, M. Behzadpour

Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad, P.O. Box: 9177948974, Mashhad, Iran

ARTICLE INFO

Article history:
Received: 07 May 2019
Final Revised: 29 Sep 2019
Accepted: 01 Oct 2019
Available online:07 Dec 2019

Keywords:
Alkyd Paint
Pigment
Extender
Titanium Dioxide
Kaolinite.

ABSTRACT

The main purpose of this study was to investigate the effects of different types and concentrations of mineral extenders on some major properties of long oil alkyd paint with the main pigment of titanium dioxide (TiO_2). To this end, a fraction of TiO_2 was replaced with extenders including kaolinite, talc, dolomite, and barite. Moreover, adhesion, bending test, and coating quality were measured once the given extenders were added to the formulation. The results revealed that adding these extenders to the formula had led to no significant changes in adhesion, bending test, as well as coating quality. In addition, drying time, reflection, total solvent used, milling time, and hiding power were considered as some parameters monitored during the use of different types of extenders. The findings also confirmed that replacing 5 and 7 wt.% of TiO_2 with different extenders could have an adverse effect on reflection and hiding power. However, milling time and total solvent used had increased. Moreover, samples such as kaolinite + calcium carbonate ($CaCO_3$) (H-1), kaolinite + talc (H-2) and kaolinite + nano clay (NC) (H-3) were prepared to investigate the effect of hybrid extender content on major properties of the paint. The results revealed that milling time and solvent weight had augmented and the paint including kaolinite + NC (H-3) showed the highest level of milling time (420 min) and solvent weight (63.9 g) among others. However, drying time and reflection did not show any significant difference. In addition, the findings confirmed the positive effect of the hybrid extender system on abrasion properties of the long oil alkyd paint. Prog. Color Colorants Coat. 13 (2020), 167-175© Institute for Color Science and Technology.

1. Introduction

In paint industry, alkyd paint is known as one of the most applicable coatings around the world. In fact, more than 40% of paint marketing belongs to such coatings, probably on account of some advantages of alkyd paint such as cost-effectiveness, high level of stability against ambient temperature and corrosion, and so on. This kind of paint is also widely used as a binder, a softener, a primer, a printing ink, etc. [1-5].

Alkyd paint is normally made up of some ingredients including main resin, solvent, pigment, as well as some additives such as drier and extender. Pigments are also graded into two categories of organic and inorganic ones. In this respect, the inorganic pigment provides better properties in comparison with others. In fact, the in organics show more resistance against sunlight and chemical exposure [6-10]. One of the serious challenges facing paint industry may be the costs of pigments; so, common pigments like TiO_2 are too expensive. As a result, final costs of paint formula largely depend on total content of pigments. In addition, TiO_2 may be considered as an ultraviolet

*Corresponding author: ramezanian@um.ac.ir

(UV) frequency absorber that results in a decrease in useful life of paint films [11-13].

The vital role of extenders in paint formula can thus reduce costs via replacing them with a fraction of main pigments. Beside the mentioned roles, extenders may result in raising the final volume of paint and improve its viscosity, adhesion, hardness, gloss, etc. In addition, talc and kaolinite are well-known minerals utilized as extenders whose most important advantages might be improving adhesion and preventing paint films against water permission and corrosion [14-17]. In this respect, Chukwujike et al. studied the effect of different particle sizes (0.075, 0.15 and 0.3 mm) of clay extenders on major properties of alkyd paint [18]. This experiment showed that using clay extenders had resulted in increased viscosity. However, alkyd paint including 0.075 mm clay particle size had low drying time compared with 0.15 and 0.3 mm clay particle sizes.

Application of chemically-treated kaolinite in comparison with natural and calcined kaolinite as steel protection in medium alkyd paint have been also investigated [19]. In this regard, chemically-treated kaolinite had been prepared via converting γ-Al_2O_3, naturally found in kaolinite, into α-Al_2O_3 through ammonium molybdate. Accordingly, the results had revealed that; among three different types of kaolinite, the calcined one has been endowed with more positive performance in steel protection than two others.

The main purpose of this experiment was to find the best replacement for TiO_2 with a cost-effective formulation of alkyd paint. In fact, some major properties of this kind of paint such as reflection and hiding power were measured once different types and concentrations of extenders including kaolinite, dolomite, talc, and barite were used.

2. Experiment

2.1. Materials

Long oil alkyd resin was purchased from Jahan Shimi Baspar Co. (Tehran, Iran). Moreover, titanium dioxide (TiO_2) as the main pigment was bought from Kosar Co. (Tehran, Iran), dolomite and kaolinte in commercial grades were purchased from Pars Kaolin Co. (Tehran, Iran), and hydrated magnesium silicate with the trade name of talc was bought from Rahpouian Sanat Lidoma Co. (Yazd, Iran). Barium sulfate was also bought from Persian Gulf Powdersazan Co. (Isfahan, Iran). In addition, petroleum solvent was used in the formulation.

2.2. Equipment

A mixer (LG Co., Korea), a film applicator (Neortek Co., USA), a 0.0001 electronic digital scale (120 BL, Sartorus Co., Germany), a grindometer (Eeichsen Co., Germany), a gloss meter (Novo Co., UK), a cross hatch cutter (ZMG 2151, Zehntner Co., Germany), and a conical mandrel bend tester (Gotech Co., Germany) were used to evaluate paint adhesion. Moreover, Taber Abrasion Tester TF214 (made in China) and thickness meter (BREIVE Co., Belgium) were employed.

2.3. Paint preparation

In order to prepare alkyd base paint, long oil alkyd resin was utilized. Some major properties of this paint and the percentages of each ingredients are listed in Tables 1 and 2, respectively. In addition, TiO_2 as pigments and some minerals as extenders were utilized in the formula (Table 3). In order to analyze the prepared paint some substrates were formed. Glass substrate (for the bending test, drying time, and glossiness) and metal sheet (for the abrasion test) in proportion of 5×15 and average thickness of 0.9 mm was also used. A prepared paint film was subsequently left on the glassy substrate via an applicator (thickness of 100 micron). Additionally, spray equipment was used to coat the metal sheet.

2.4. Process

At first, a fraction of alkyd resin was added into the mixer whose revolutions per min (rpm) was set on 270. Then, the total volume of pigments and extenders (based on the formula in Table 4) were gradually added into the mixer. The mixture was blended for about 15 min. In order to mill the pigments and the extenders completely, pearl mill was used. Milling process also continued until the particle size reached 15-20 micron [20].

At this step, the rpm of the mixer increased from 270 to 420. Once the mixture reached the desired particle size, the remaining fraction of the alkyd resin with other additives such as the solvent was also added to the mixture.

Table 1: Main properties of the used paint.

paint properties	value
resin base	Long oil alkyd (soy bean fatty acid)
density (g/cm^3)	0.93
solid content (%)	59-61
viscosity(st)	350-450
acid value (mg KOH/g)	6-10

Table 2: Ingredients of the used paint.

Ingredients	Value (%)
alkyd long oil resin	41.85
Emulsifier (lecithin soy)	0.20
pigment	16.08
filler	13.38
bentonite gel	1.90
drying agent (Co)	0.38
drying agent (Ca)	0.67
drying agent (pb)	0.30
anti-skinning agent	0.28
solvent	24.96
total	100

Table 3: Main characteristics of dolomite, kaolinite, talc, and titanium dioxide.

characters	dolomite	talc	TiO_2	kaolinite	barite
appearance	white powder	white powder	white powder	white powder	white powder
chemical name	Anhydrous carbonate mineral	hydrated magnesium silicate	titanium dioxide	-	barium sulfate
chemical formula	$CaMg(CO_3)_2$	$H_2Mg_3(SiO_3)_4$	TiO_2	$Al_2Si_2O_5(OH)_4$	$BaSO_4$
particle size (μm)	-	25-30	0.3	-	3
density(g/cm^3)	2.85	2.6-2.8	-	-	4.48(2.15)
pH	-	7-9	-	6-7	6.5

Table 4: Replacement percentages of extenders in paint formula.

sample code	alkyd paint content (wt.%)	TiO_2 (wt.%)	Kaolinite (wt.%)	Talc (wt.%)	Dolomite (wt.%)	Barite (wt.%)
SP-0	50	50	-	-	-	-
SP-1	50	45	5	-	-	-
SP-2	50	45	-	5	-	-
SP-3	50	45	-	-	5	-
SP-4	50	45	-	-	-	5
SP-5	50	43	7	-	-	-
SP-6	50	43	-	7	-	-
SP-7	50	43	-	-	7	-
SP-8	50	43	-	-	-	7

2.5. Characterization

The Institute of Standards and Industrial Research of Iran (ISIRI) 1700 was used to calculate drying time and the coating quality of the solvent paint [20]. Reflection and hiding power of the alkyd paint was also determined based on the ISIRI number 6460 and International Organization for Standardization (ISO) 2418 [21, 22]. Moreover, the bending test was controlled according to [23]. Additionally, paint adhesion [24] and abrasion resistance [25] were measured by using appropriate references.

3. Results and Discussion

In order to investigate the effect of different extenders, some qualitative and quantitative tests were selected and carried out. The results of some analyses including adhesion, coating, and bending test are shown in Table 5. In this experiment, the sample code of SP-0 was used as the reference. Using 5 and 7 wt.% of different extenders, the results of adhesion and bending test remained almost constant. In addition, coating test illustrated the same results through the replacement of a fraction of the main pigment with different extenders (5 wt.%) in comparison with the reference results (SP-0). However, increasing the percentage of the extender from 5 to 7 wt.% led to a decrease in the level of coating quality for kaolinite, talc, and dolomite (SP-6, SP-7, and SP-8).

Drying time is taken into account as one of the major properties in paint industry. In this experiment, drying time of different formulations was measured based on total time in which paint film with the thickness of 30 micron needed to dry completely.

The effect of different types and replacement percentages of extenders on drying time is also demonstrated in Figure 1. The drying time of the reference was about 630 min and the results confirmed that replacing 5 wt.% of TiO_2 with kaolinite, talc, and barite had brought about a significant improvement in the drying time from 630 (for SP-0) to 660 min. However, in the formula containing dolomite as an extender, the drying time was about 630 min (almost constant). In addition, the time did not change remarkably using 7 wt.% of the extender in paint formulation in comparison with the samples with 5 wt.% replacement.

Table 5: Effect of different extenders on adhesion, bending test, and coating quality.

sample code	adhesion	coating	bending test (+/-)
SP-0	5B	very good	+
SP-1	5B	very good	+
SP-2	5B	very good	+
SP-3	5B	very good	+
SP-4	5B	very good	+
SP-5	5B	Acceptable	+
SP-6	5B	Acceptable	+
SP-7	5B	Acceptable	+
SP-8	5B	very good	+

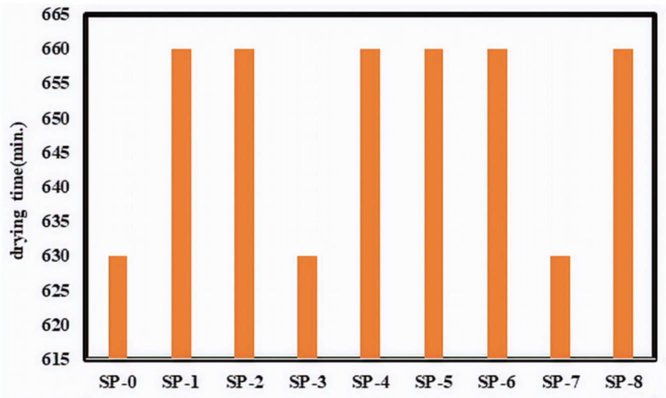

Figure 1: Effect of replacement percentages on paint drying time.

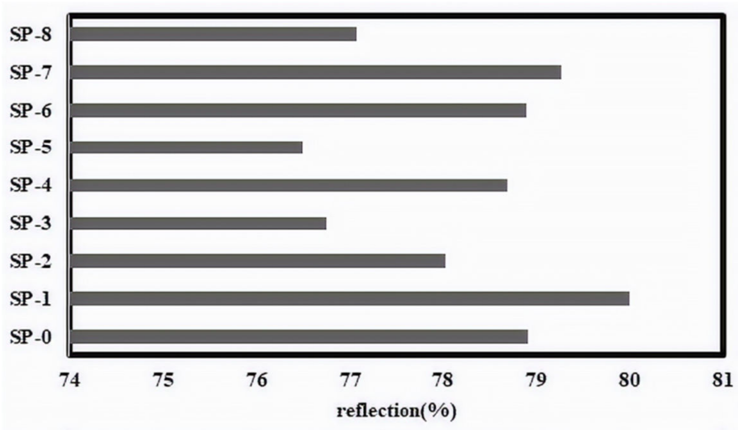

Figure 2: Effect of different types and concentrations of extenders on prepared paint reflection.

Reflection percentage is known as a parameter in which opacity or glossiness of paint can be determined in a way that the greater the percentage of the reflection, the higher the glossiness of the paint. Investigations into effects of different extenders on reflection of alkyd paint have also demonstrated that changing extenders could significantly influence reflection percentage (Figure 2). In fact, compared with the reference, reflection percentage in this study could improve from 78.92% to approximately 80%, using 5 wt.% of kaolinite. However, talc and dolomite led to a slight decline in reflection from 78.92 to 78.03 and from 78.92 to 76.75, respectively. In addition, reflection percentage remained almost constant while the main pigment was replaced with 5 wt.% of the barite. Raising the replacement percentage of the extender from 5 to 7 wt.%, reflection of the samples with kaolinite and barite had a significant decrease from 78.92 to 76.5 and from 78.92 to 77.08, respectively. Moreover, talc and dolomite did not cause remarkable changes in terms of reflection.

Solvents are typically used in order to homogenize all paint components. In addition, total volume of solvents needed for each mixture depends on compatibility of ingredients. Therefore, improving compatibility of paint components including pigments, extenders, etc. can significantly reduce total volume of solvents as well as average milling time. In this study, petroleum solvent was utilized until paint viscosity reached an acceptable range (80-105 Krebs). The effect of different extenders on solvent volume used for each formula is illustrated in Figure 3. The results showed that the total volume of the solvent had significantly increased from 40 g (for reference) to 51 g and from 40 to 45 g, respectively, replacing 5 wt.% of TiO_2 with kaolinite and dolomite. However, the solvent used did not change once barite and talc were replaced with the main pigment. Moreover, improving replacement percentage from 5 to 7 wt.% could significantly increase the total solvent used for the formula which included talc (41.2%). In addition, utilizing kaolinite and dolomite resulted in raising the solvent volume in the formula (30 and 25%, respectively). Nevertheless, the total volume of the solvent did not change on purpose as TiO_2 was replaced with barite.

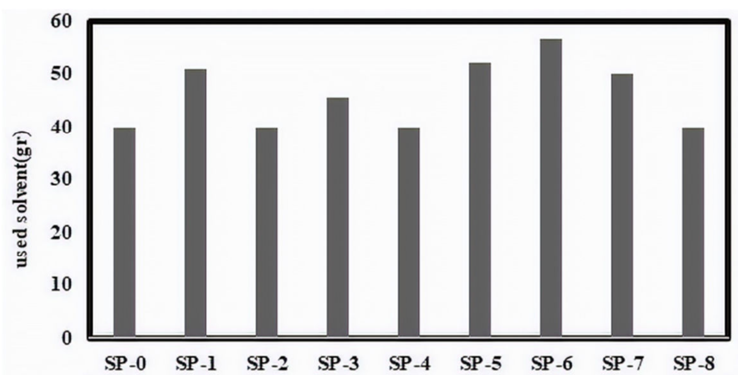

Figure 3: Changes in total solvent used for each formula.

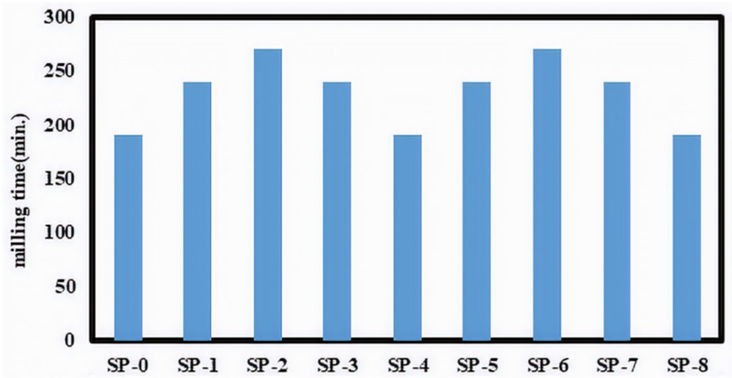

Figure 4: Milling time vs. percentage replacement of extenders.

As mentioned above, the type and the ratio of each ingredient in paint formulation had a direct effect on average milling time to achieve an acceptable range of particle size (15-20 micron) [20]. In this experiment, the milling time was measured for each formulation based on types and concentrations of the extenders (Figure 4). The results also revealed that average milling time for the reference was equal to 200 min. In addition, the milling time significantly increased following the replacement of 5 wt.% of the TiO_2 with extenders, except for barite. In fact, the milling time of the alkyd paint containing barite did not change. Using 7 wt.% of the extenders, the same results were further achieved. In other words, improving the replacement percentage did not have any effects on milling time.

The amount of hiding power for different formulations of alkyd paint is shown in Figure 5. In other words, it seems that different replacement percentages of the extenders had a significant effect on hiding power. Moreover, the results confirmed that the reference with the code of SP-0 had a hiding power, i.e. about 11 m^2/L. In addition, this parameter decreased in a significant manner from 11 to 9 m^2/L; once the extender of dolomite was replaced with 5 wt.% of the main pigment in the formula. However, the hiding power improved and reached 12 m^2/L, using talc as a mineral extender. Additionally, the hiding power of the paint did not change while kaolinite and barite were used. Raising the replacement percentage from 5 to 7 wt.% also caused a sharp decline in the hiding power of the paints having kaolinite, talc, and dolomite in their formula. Nevertheless, replacing TiO_2 by 7 wt.% with barites made the hiding power remain constant.

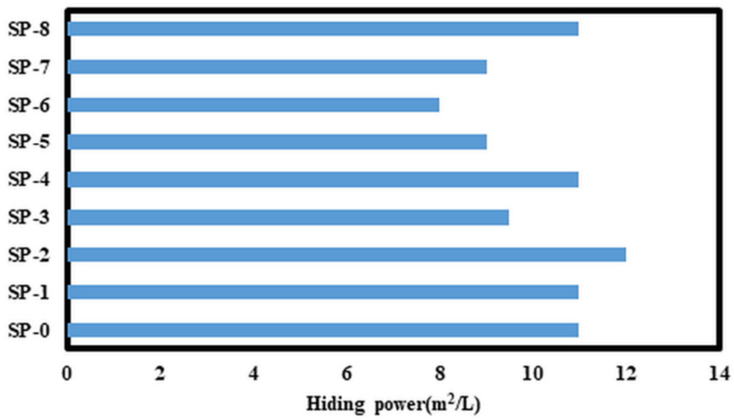

Figure 5: Hiding power of different formulas.

3.1. Hybrid extender system

Samples such as H-1, H-2 and H-3 were prepared to estimate the effect of the hybrid extender content on major properties of the alkyd paint. The extender content of these samples is demonstrated in Table 6.

The results confirmed (Table 7) the significant influence of hybrid extender content on alkyd paint properties. In fact; adding 3 wt.% calcium carbonates (H-1), talc(H-2), and NC(H-3) to 5 wt.% of kaolinite led to an increase in the milling time from 180 (SP-0) to 270.300 and 420 min, respectively. The drying time, however, did not show a significant influence.

Total solvent weight had also sharply increased when using H-2 and H-3 extender systems. In addition, application of hybrid extender including kaolinite and NC could decrease paint reflection from 78.92 to 75.82; while, H-1 and H-2 did not significantly change the reflection.

The abrasion resistance of the hybrid extender system was also determined (Figure 6) and the improvement in the resistance of the paint-containing hybrid extender in comparison with SP-0 was confirmed. In fact, the H-1 and H-2 samples showed the same abrasion resistance (~37g^{-1}); while, use of kaolinite and NC as extenders (H-3) caused a sharp enhancement in the abrasion resistance of the paint (+33%).

Table 6: Extender content in hybrid extender of alkyd paint.

Sample code	Extenders content
H-1	Kaolinite (5 wt.%) + calcium carbonate (3 wt.%)
H-2	Kaolinite (5 wt.%) + Talc (3 wt.%)
H-3	Kaolinite (5 wt.%) + nano clay (3 wt.%)

Table 7: Effect of hybrid extender content on major properties of alkyd paint.

Sample code	Reflection (%)	Milling time(min.)	Used solvent (g)	Drying time(min.)
SP-0	78.92	180	40	630
H-1	78.85	270	40	650
H-2	79.96	300	54.1	630
H-3	75.82	420	63.9	650

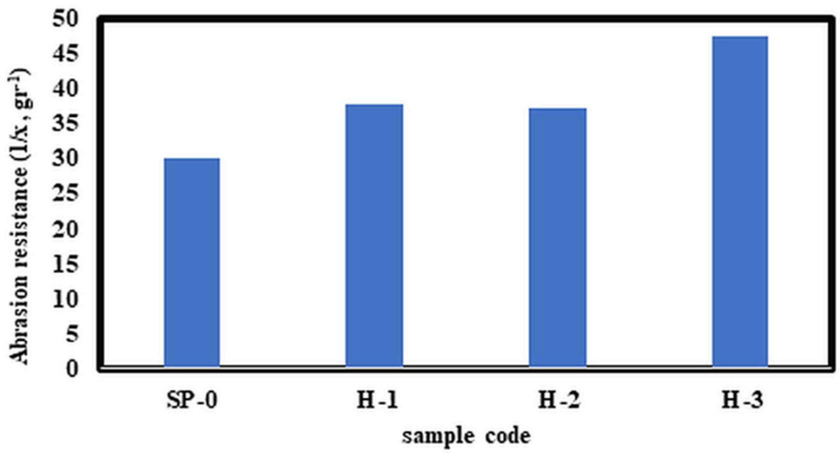

Figure 6: Influence of hybrid extender content on abrasion resistance of alkyd paint.

4. Conclusion

This study investigated the effect of different types of extenders on major properties of long oil alkyd paint. The extenders replaced with the main pigments (TiO_2) were kaolinite, talc, dolomite, and barite. Accordingly, the results revealed that adding 5 and 7 wt.% of the extenders in the formula had not remarkably changed adhesion, bending test, and coating quality. In fact, all results were in an acceptable range. In addition, the drying time of the paint containing different contents of the dolomite did not change and it was almost equal to the reference (namely, 630 min). However, other extenders brought about an increase in the drying time from 630 to 660 min.

Measuring the reflection of the samples showed that using 5 wt.% of the extenders had caused decrease in the reflection of the paint, except for kaolinite. Moreover, raising the extender contents of kaolinite and barite from 5 to 7 wt.% had led to a decline in reflection from 78.92(reference) to 76.5 and from 78.92 to 77.08, respectively. The total volume of the solvents used for reference was about 40 g. However, the volume of the solvent needed had slightly increased once 5 wt.% of kaolinite and dolomite had been added. Furthermore, talc and barite did not significantly change the solvent volume. Utilizing 7 wt.% of kaolinite, talc, and dolomite; the total volume of the solvent increased.

As the main pigment was replaced with 5 and 7 wt.% of kaolinite and dolomite, the milling time of the paint increased intentionally from 200 (reference) to 240 min. Moreover, the milling time improved and reached 260 min using talc as an extender. Nevertheless, barite did not have a significant effect on milling time.

Measurements confirmed that the hiding power of the reference sample was approximately 11 m^2/L. In addition, replacing 5 wt.% of TiO_2 with kaolinite and barite did not change the hiding power of the paint. However, the hiding power varies from 11 to 12 m^2/L once 5 wt.% of talc was replaced with TiO_2. Moreover; addition of dolomite (5 and 7 wt.%), kaolinite (7 wt.%), and talc (7 wt.%) resulted in a decrease in the hiding power. Consequently, it seems that the prepared paint (SP-8, including barite as a extender) showed more acceptable results especially in the solvent used (40 g), milling time (160 min), and hiding power (11 m^2/L) in comparison with other formulations.

Samples were prepared (H-1, H-2 and H-3) to estimate the effect of hybrid extender content on major properties of the alkyd paint. Milling time and solvent weight had further increased. Besides, the paint including kaolinite + NC (H-3) showed the highest level of milling time (420 min) and solvent used (63.9 g) among others. However, drying time and reflection had not remarkably changed. In addition, the results demonstrated the positive effect of the hybrid extender system on the abrasion properties of the alkyd paint.

Acknowledgment

This work was supported by Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad (project code: 3/46659), Mashhad, Iran and Orkideh Toos paint and resin Co. Mashhad, Iran which are greatly appreciated.

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How to cite this article:

F. Tahmasb Pour Afshar, N. Ramezanian, M. Behzadpour, Identification and Evaluation of Replaced Materials of Titanium Dioxide Pigment in Alkyd Resins and Investigation of their Properties. Prog. Color Colorants Coat., 13 (2020), 167-175.