CHAPTER IV

RESULTS AND DISCUSSION

This research was concerned with the elaboration of new 100% acrylic emulsion paint with special features of excellent flame retardant and antifungal properties.

Flame retardant properties could be improved by the addition of metal hydroxide and APP. In the past, ATH was used in plastic materials with higher content (more than 30%) to achieve the acceptable OI (more than 26%) [3]. APP was used in paint by the combination with other 2 agents: spumific agent (melamine) and carbon char resource (pentaerythritol) to get the intumescence to protect the substrate from fire. In fact, many ways to achieve the flame retardant property in paint were addressed. For example, Gunduz *et al.* [3] increased the OI of long oil alkyd paint by incorporation with *bis*-pyridine *bis*-tribromophenoxocopper (II) complex and poly-dibromophenylene oxide (PDBPO). Because of good advantages of ATH and APP, this research was thus focused on the utilization of both ATH and APP in combination. The aim to use these components was to reduce the content of ATH and to avoid using the spumific agent and pentaerytritol. For antifungal property, new fungicides blending in 100% acrylic emulsion paint would be examined. The flame retardant property and fungal resistance were evaluated by oxygen index (OI) according to ISO-4589 Part 2 and TISI. 285 Volumn 21, 1982, respectively [15].

4.1 Effect of metal hydroxide and APP

ATH was used in the solvent base paint such as long oil alkyd and was studied the effect on flame retardant property in the plastics materials such as thermoplastics polyurethane (TPU) elastomers by *Pinto et al,* ATH at 70 and 80 phr mixing in TPU were used and OI was found to significantly increase. [6]

Metal hydroxide such as ATH has a few mechanisms as flame retardant: to reduce in thermal decomposition and to release the large amount of water during the decomposition process to promote the heat absorption. APP, on the other hand would decompose and form non-flammable product such as polyphosphoric acids when a fire breaks out.

$$(NH_4)_3PO_4 \xrightarrow{>150^oC} H_3PO_4 + 3NH_3$$

This research was tried to compare the OI of existing product with that of the product blending with 16% ATH content. Another set of OI observation would make with the formulations containing 10 and 20% of APP by weight.

4.2 Oxygen index value (OI value)

Oxygen index is the minimum concentration of oxygen that requires to combustion process. The specimens were conditioned at 23°C and 50%RH for at least four days prior to testing [20]. OI measurement was determined according to ISO 4589 Part 2 (OI value of each formula was showed at the testing machine). The flame was applied to the top of the specimens using a sweeping motion for continuous period of 30 seconds without any removal of the flame. Polymer with OI more than 26% is considered to be a flame retardant in terms of self-extinguishing 3]. Every paint formulation,OI value was got from fire testing technology (FTT) oxygen index apparatus. OI measurement of three diverse formulations composing of TiO_2 : kaolin : APP and ATH was collected in Table 4.1 with the aim to observe the effect of ATH content on OI value at containing 26% total filler content.

Table 4.1 Effect of ATH and APP content on OI value

Formulation	TiO_2 : Kaolin : APP : ATH	Flame retardant filler content (%)	OI value (%)
Existing product	22 : 4 : 0 : 0	0	20.33
Formulation **2**	16 : 0 : 10 : 0	10	23.25
Formulation **3**	6 : 0 : 20 : 0	20	23.73
Formulation **5**	10 : 0 : 0 : 16	16	23.21

It was clearly seen that ATH and APP greatly affected on the OI values. The addition of ATH 16% enhanced the OI value from 20.33% of existing product to 23.21% of the formulation **5** (ATH content 16%) (Fig 4.1 a). In the case of APP, the addition of APP 10% revealed a pronounce effect on the increment of OI value approximately 15%. Adding 20%APP did however not show significant increase of OI value.

Nevertheless, the OI values obtained from the formulations **2**, **3** and **5** revealed the figure less than 26% which was not acceptable as flame retardant. Thereby, the attempt to raise up this value was performed by combining ATH and APP with the aim to see the synergist effect. All experiments were carried out at the same total filler content as in the existing product (26%) and the same total.

The effect of combined ATH and APP at 20% flame retardant filler content on the OI value was presented in Table 4.2.

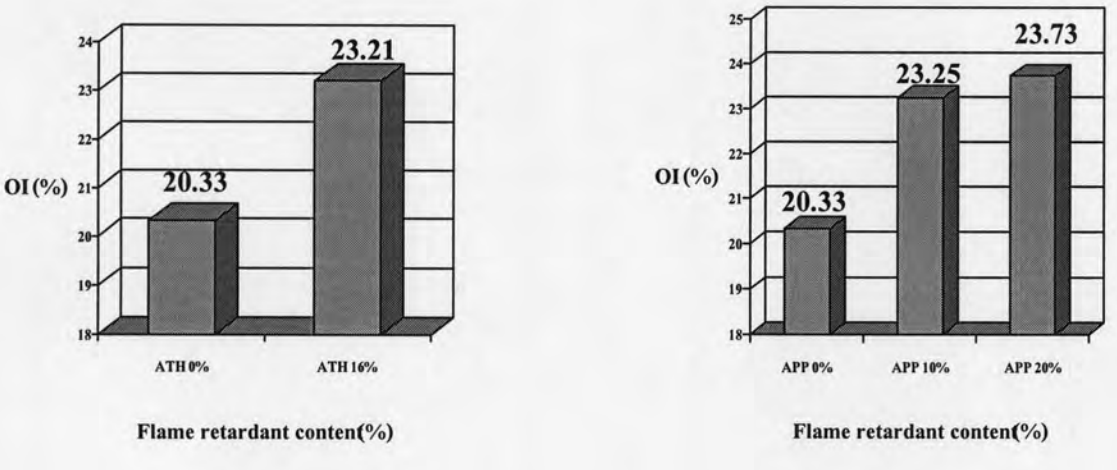


Fig. 4.1 The effect of a) ATH and b) APP on OI value

Table 4.2 Synergist effect of APP and ATH at 20% flame retardant filler content

Formulation	TiO_2 : Kaolin : APP : ATH	OI value(%)
Existing product	22 : 4 : 0 : 0	20.33
Formulation **3**	6 : 0 : 20 : 0	23.73
Formulation **4**	6 : 0 : 10 : 10	24.44
Formulation **6**	6 : 0 : 10 : 10	24.23

*For every formulation studied, OI test results were not different for 2 times of testing.

From Table 4.2, formulation **4** displayed an interesting result. The OI value was raised up to 24.44, possibly by the synergist effect between APP and ATH.

Formulation **6** was compared with formulation **4** to study the effect of pentaerytritol without spumific agent using for intumescent paint. It was found that pentaerytritol did not show any effect on OI value.

The new paint formulae with 26% total filler content cannot however improve the flame retardant property. Thus, increasing the total fillers content was next parameter to be considered. 40% Total filler contents with the ratio of TiO_2:APP of 10:30 and TiO_2:APP:ATH of 10:25:5 and 10:20:10 were conducted to observe the synergist effect. The findings are displayed in Table 4.3.

Table 4.3 OI values of paint with different filler contents

Formulation	TiO_2 : Kaolin : APP : ATH	OI value(%)
Existing product	22 : 4 : 0 : 0	20.33
Formulation **7**	10 : 0 : 30 : 0	29.30
Formulation **8**	10 : 0 : 25 : 5	32.13
Formulation **9**	10 : 0 : 20 : 10	33.81

The OI values of formulations **7** and **8** are quite impressive, increasing from 20.33% to 29.30, 32.13%, respectively. These two paint formulations were accepted to display flame retardant property. The main influence for this better result was

stemmed from the synergist effect of APP and ATH. At the same total filler content 40%, a new formulation **9** was prepared by increasing ATH content from 5% in formulation **10** to 10% in formulation **9.** This formulation provided very good OI value of 33.81% Nevertheless, the higher filler content in paint formula would reflect to physical property consequently, the next two formulas were prepared by lowering total filler content to 35% and 30%.

Table 4.4 OI value of paints at 35% and 30% total filler content

Formulation	TiO_2:Kaolin: APP:ATH	Total Filler (%)	Flame retardant filler content(%)	OI value (%)
Existing product	22 : 4 : 0 : 0	26	0	20.33
Formulation **10**	10 : 0 : 10 : 15	35	25	28.52
Formulation **11**	10 : 0 : 10 : 10	30	20	26.65

Decreasing total filler content from 40% (in formulations **7, 8** and **9**) to 35% (formulation **10**) and 30% (formulation **11**) resulted in OI value of 28.52% and 26.65%, respectively. These two formulations **10** and **11** displayed the flame retardant property.

4.3 Effect of titanium dioxide to OI value

TiO_2 exhibited its effect on OI value. This could be observed from certain formulations such as formulations **4** and **11.** To illustrate this, these two formulations with the same content of APP and ATH, but different in the amount of TiO_2 from 6% to 10% revealed different OI values as presented in Fig. 4.2.

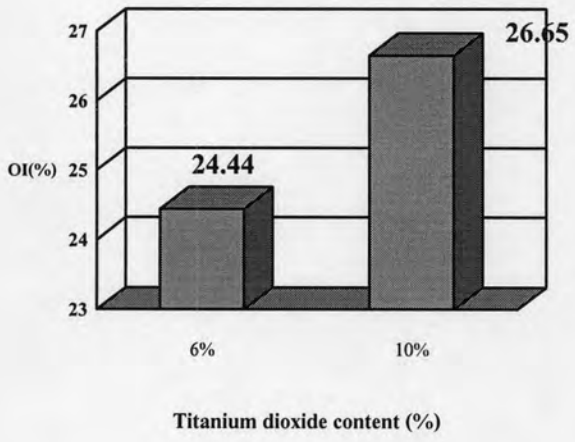


Figure 4.2 Effect of TiO_2 on OI value.

From the total paint formulations, it could be observed that the OI value increased when increasing the amount of flame retardant filler. This could be seen from the comparison study at the same content of 10% TiO_2 such as formulations **5** (16% ATH), formulation **11** (20% APP:ATH), formulation **10** (25% APP:ATH), formulation **7** (30% APP), formulation **8** (30% APP:ATH) and formulation **9** (30% APP:ATH) OI values are shown in Fig. 4.3.

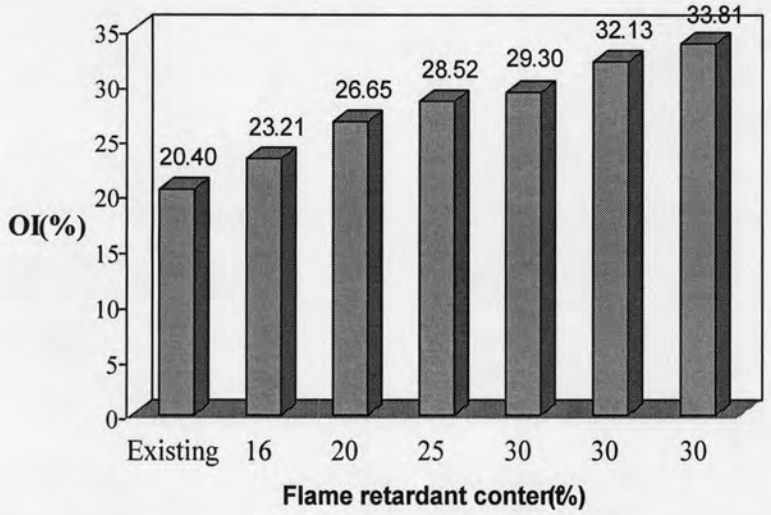


Figure 4.3 The effect of flame retardant filler content on OI value.

Remark : Formulation **7,8** and **9** were different in the ratio of APP:ATH.

4.4 Physical properties of flame retardant acrylic emulsion paints.

APP is a good flame retardant filler and good water solubility and poor hiding power so the paint formula with high content of APP will have some disadvantages in water resistant and poor opacity. Table 4.5 shows paint properties comparing each formulation. All properties were tested by ICI test method (ATM; Asia Decorative Product Test Method).

Table 4.5 Physical properties of flame retardant paints.

Specification	Flame retardant formulation						
	Existing	2	3	4	5	6	STD.
1. Viscosity (Ps.,RT.,25°C)	7.9	7.6	7.2	7.8	6.9	6.8	7.0-8.5
2. Opacity (%)	96	93	82	83	88	90	88% Min.
3. Weight per gallon	4.735	4.782	4.504	4.5779	4.650	4.831	4.713-4.905
4. Fineness (Microns)	<30	<30	<30	<30	<30	<30	30-35
5. Washability	Pass	Pass	Pass	Pass	Pass	Pass	Cleaned
6. Bending test	Pass	Pass	Pass	Pass	Pass	Pass	No peel
7. OI (%)	20.33	23.25	23.7	24.44	23.21	24.25	26%Min.
8. Water resistant(18 Hrs.)	Pass	Pass	Blistering	Slightly	Slightly	Slightly	No blistering

Table 4.5 (continued)

Specification	Flame retardant formulation							
	Existing	7	8	9	10	11	12	STD.
1. Viscosity (Ps.,RT.,25°C)	7.9	9.2	9.4	9.5	8.5	8.2	8.3	7.0-8.5
2. Opacity (%)	96	88	92	91	92	90	92	88% Min.
3. Weight per gallon	4.735	4.892	4.780	4.812	4.620	4.655	4.892	4.713-4.905
4. Fineness (Microns)	<30	<30	<30	<30	<30	<30	<30	30-35
5. Wash ability	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Cleaned
6. Bending Test	Pass	Pass	Pass	Pass	Pass	Pass	Pass	No Peel
7. OI (%)	20.33	29.3	32.13	33.81	28.52	26.65	-	26% Min.
8. Water resistant (18 Hrs.)	Pass	Blistering	Blistering	Blistering	Slightly	Slightly	Slightly	Pass

4.4.1 Effect of total filler content to paint viscosity

From Table 4.5, the viscosity of paints was increased when increasing the total filler content. As presented in Fig. 4.4, the filler content was varied from 26%, 30%, 35% and 40%. For the paint manufacturer in the case of the viscosity being lower than standard specification, the addition of thickening agent was required. On the contrary, if viscosity was too high, it can be adjusted by adding water.

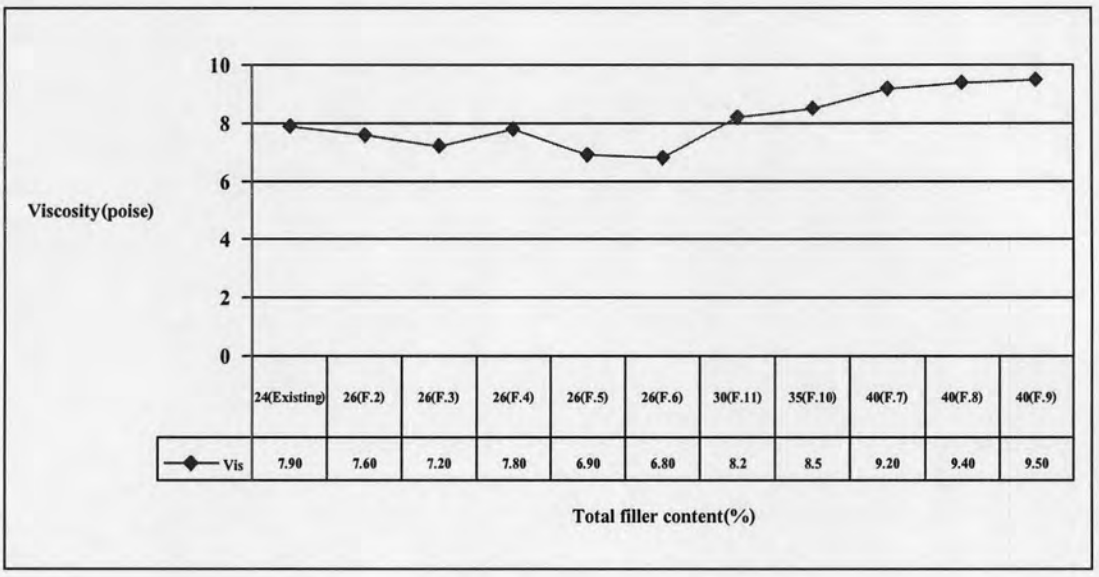
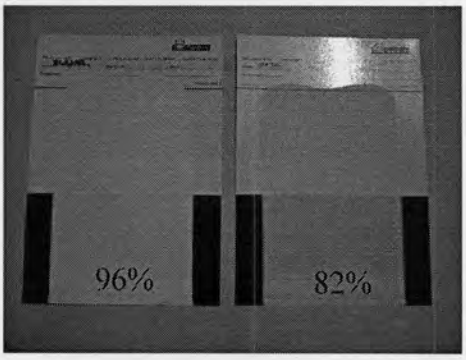


Figure 4.4 The effect of total filler content on viscosity.

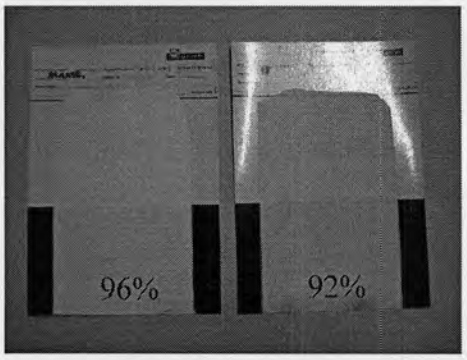
At total filler content 24%-35%, the viscosity of paint was in the standard range. The increasing of paint's viscosity occurred when the total filler was up to 40% in formulations **7, 8** and **9**.

4.4.2 Effect of titanium dioxide content to opacity.

Opacity results the identity of the hiding power of paints to substrate. Good paints should have higher opacity value to conceal the substrate as shown in Fig.4.5b. On the contrary, the lower opacity paint cannot conceal the substrate as in the Fig.4.5a. TiO_2 was the filler in paint that showed good hiding power property. From Table 4.5, opacity was decreased when the content of TiO_2 was reduced (Fig. 4.6). The optimum TiO_2 content in new paint formula should not be less than 10% to achieve the opacity value more than 88%.



a) Existing & Formulation **3**.



b) Existing & Formulation **10**.

Figure 4.5 Opacity samples of existing compare with developed formulations.

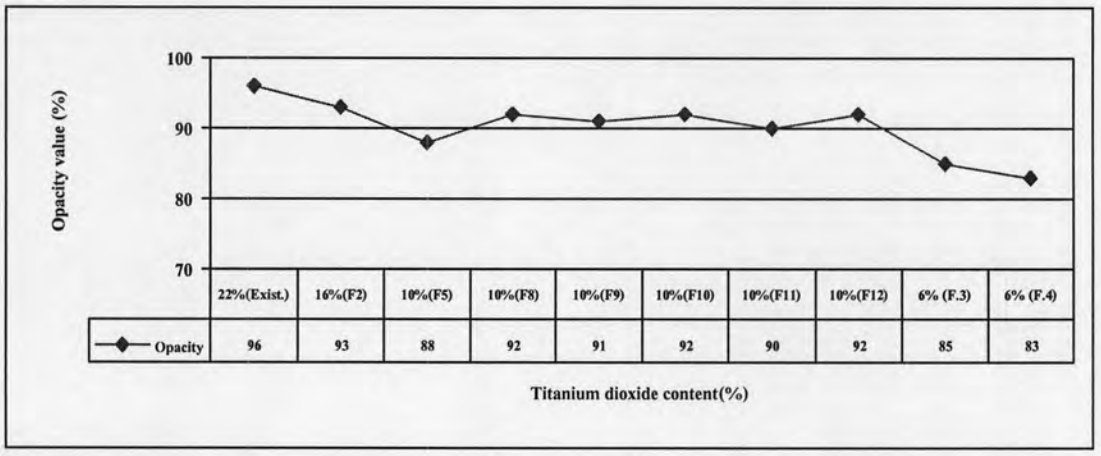


Figure 4.6 Effect of TiO_2 content on opacity value.

4.4.3 Effect of flame retardant filler content on water resistance property

APP has good water solubility property. When it was used in paints, the water resistance property was dropped. From Table 4.5, formulations **8** and **9** showed good flame retardant property with OI more than 30%. Nevertheless, after testing for water resistance property by dipping into water for 18 hrs, the blistering problem was observed. When the formulation was developed by reducing the APP content from 25% and 20% to 10%, it was found that the water resistance property was improved and still showed the flame retardant property with OI 28.52% in formulation **10**.

4.5 New fungicides for 100% acrylic emulsion paint

In the past, the common antifungal generally used in emulsion paints were IPBC and MIT [14] which displayed good activity against *Aspergillus niger* and *Penicillium funiculosum, etc.*

In this research, the antifungal activity was tested against *Aspergillus ni*ger following TIS 285 Volumn 21, 1982.[15] Propyl 4-hydroxybenzoate and 2,4-dichloro-cinamic acid are new antifungal agents.[16] Captan is widely used to protect seeds and field crops while iprodione was used to protect fruits, vegetables and grasses. [17] Berbirine chloride, a new anti-pathogenic fungal agent displayed good antifungal property against *Alternaria porri, Cercospora sp., Colletotrichum gloeosporioides, Fusarium oxysporum, Phytophthora parasitica and Pythium deliense,* causing disease in many Thai crops.[18] These agents have never been used in paint before; thus these new fungicides containing in 100% acrylic emulsion paint would be examined.

4.6 Anti-fungal test result

Agar plates were incubated at 28-30°C, 85-90%RH and evaluated the fungi growth in the focus area. Following TISI test method, it was reported only as found or not found the fungal on paint film panel. This research tried to compare the efficiency of each formula, so the result would be reported in terms of scales 0-5 following Troy's testing method. These scales show the density of *Aspergillus niger* on the sample panel from 0-100%.

Table 4.6 Growth scale result of *Aspergillus niger* on paint film.

Formulation/Antifungal	Growth Scale
1.Standard / Zinc omadine	0 (Fig. 4.8)
2.Anti-**2** / Propyl 4-hydroxybenzoate at 0.5%	4 (Fig. A2)
3.Anti-**3** / Propyl 4-hydroxybenzoate at 1.0 %	5 (Fig. A3)
4.Anti-**4** / Berberine chlorine	4 (Fig. A4)
5.Anti-**5** / Captan at 0.5%	1 (Fig. 4.6)
6.Anti-**6** / Iprodione	3 (Fig. A5)
7.Anti-**7** / 2,4-Dichlorocinnamic acid	5 (Fig. A6)
8.Formulation **12**/ Captan at 1%	0 (Fig. A6)

Remarks :

- 0 = No growth on the film surface, zone of inhibition may be present
- 1 = Trace of growth on test sample (<5%)
- 2 = Light growth on test sample (6-25%)
- 3 = Moderate growth on test sample (26-75%)
- 4 = Heavy growth on test sample (76-99%)
- 5 = Very heavy growth on test sample (100%)

The anti-fungal test results followed the order of existing antifungal (zinc omadine) as similar as formulation **12** > anti-**5** > anti-**6** > anti-**4**, anti-**2** > anti-**3**, anti-**7**.

The increasing of captan content from 0.5% (anti-**5**) to 1.0% (formulation **12**) revealed that, formulation **12** was as good as the existing material (zinc omadine) and showed the best result when comparing with tested reagents. The good antifungal activity in paint could be seen from the inhibition zone around the paint film (Fig. 4.7 and Fig. 4.8). For anti-**5** containing 0.5% captan, the inhibition zone did not appear.

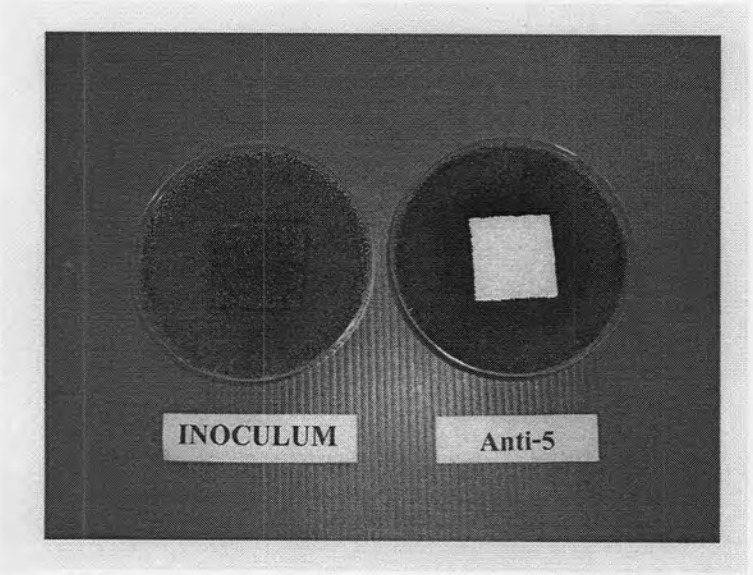


Figure 4.7 Antifungal test of anti-**5** (0.5% captan)

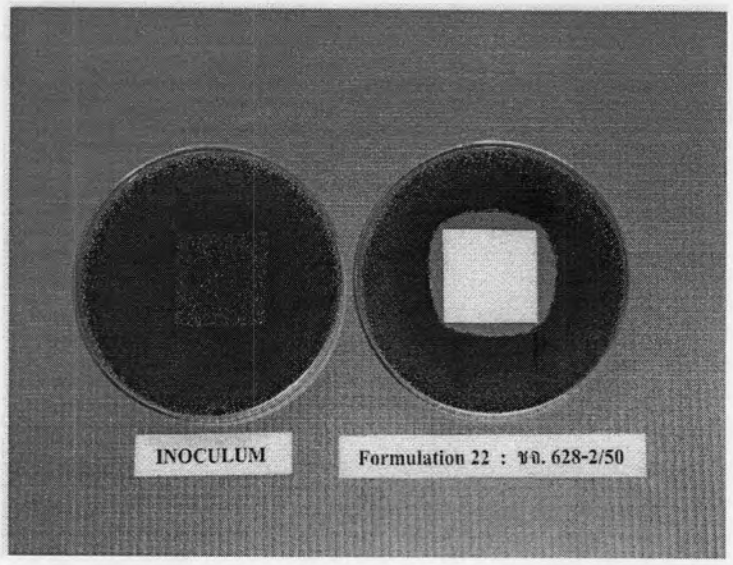


Figure 4.8 Antifungal test of formulation 12 (1.0% captan)

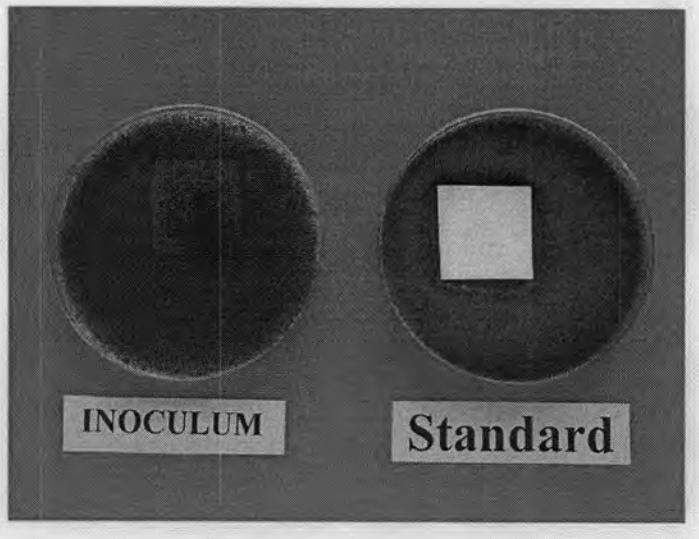


Figure 4.9 Antifungal test of zinc omadine

4.7 Physical properties of new anti-fungal acrylic emulsion paints

All properties were tested according to ICI test method (ATM; Asia Decorative Product Test Method) and are recorded in Table 4.7. The results focused not only for the antifungal property, but also the physical appearance such as color. This is because some antifungal agents have intense color.

Table 4.7 Physical properties of paints

Specification	New anti-fungal tested acrylic emulsion paints								
	Existing	Anti-2	Anti-3	Anti-4	Anti-5	Anti-6	Anti-7	F. 12	STD.
1. Viscosity	8.1	7.8	7.6	8.1	8	7.9	7.9	8.3	7.0-8.5
2. Opacity (%)	96	96	94	96	95	96	94	92	88% min.
3. Weight per gallon	4.825	4.825	4.81	4.905	4.83	4.82	4.84	4.892	4.713-4.905
4. Finess (Microns)	<30	<30	<30	<30	<30	<30	<30	<30	30-35
5. Rolling test	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Smooth
6. Color of paint	White	White	White	Yellowish	White	White	White	White	White

From the antifungal results in 100% acrylic emulsion paint, 1%captan containing in paint revealed the best result and similar to the existing formulation containing antifungal agent. All of the antifungal reagents applied did not affect on the physical properties of paint, except for the formulation anti-**4** with berberine chloride, the yellowish paint was obtained.