J. of Korean Oil Chemists' Soc., Vol. 30, No. 3. September, 2013. 518~527 ISSN 1225-9098 (Print) ISSN 2288-1069 (Online) http://dx.doi.org/10.12925/jkocs.2013.30.3.518

코팅프로세스를 사용한 5,6-디하이드록시인돌의 산화 및 광에 대한 안정화 연구

한상근^{1,2} · 이동규^{1†}

^{1,2}충북대학교 공과대학 공업화학과, ²한국콜마 피부과학연구소 (2013년 8월 19일 접수; 2013년 9월 25일 수정; 2013년 9월 26일 채택)

Study of Stabilizing 5,6-dihydroxyindole with Coating Process Against Oxidation and Light

Sang-Keun Han^{1,2} · Dong-Kyu Lee^{1†}

 ¹Department of Industrial Engineering Chemistry, College of Engineering, Chungbuk National University, Gaesin-dong, Cheongju-si, Korea
²Skin Research Institute, Korea Kolmar Corporation, 12–11, Dukgogae-gil, Sejong-si, Korea (Received August 19, 2013; Revised September 25, 2013; Accepted September 26, 2013)

Abstract : 5,6-dihydroxyindole was easily oxidation with air and light Conditions. Availability of 5,6-dihydroxyindole was studied for hair dye as a precursor of melanin. This study used wet and dry coating process to stabilize 5,6-dihydroxyindole. In wet process used dimethicone and cyclometicone, the 5,6-dihydroxyindole had darkened through the drying process at 58°C. Wet coating process was inappropriate to stabilize the coating. In dry coating process, shea butter coating was stable until 3 days. Dextrin palmitate was most efficient ingredient to prevent oxidation by sun light and air until 7days. Oxidation test with 1.0% and 1.5% of dextrin palmitate was not different under conditions of sun light and air and was not dependent on contents. Vitamin E acetate under conditions of sun light and air, there were no significant effect in preventing oxidation.

Keywords : 5,6-dihydroxyindole, melanin, dye, hair care, dextrin palmitate

1. Introduction

Material that determines the color, melanin exists in a person's hair and skin, melanin is

the pigment that determines the color of the hair[1]. All the common plants of the natural world, the use of colored organic substances, such as chlorophyll, anthocyanins, carotenoid have melanin[2]. And to have the ability to respond to harmful environmental and ecological adaptation, the animals have the melanin in the cells in order to defend the

⁺Corresponding author

⁽E-mail : dklee@cbnu.ac.kr)

ultraviolet[3]. The melanin has synthetic function of the molecular weight of the organic matter[4]. That exist in a person's skin, hair was divided into eumelanin of black and pheomelanine of vellow. Melanin is synthesized in the molanosome which organelles within melanocytes. and implemented to keratinocytes through dendrite of melanocytes[5]. Subsequent auto-oxidative reactions in the melanin synthesis pathway, tyrosine oxidation of tyrosine to DOPA and DOPA to dopa quinone is generated by the oxidation step of. It is known to accelerate progress with the presence of the enzyme. On the other hand, in order to prevent the transmission of ultraviolet light or to mute the naturally occurring active oxygen and free a person's body or hair create radicals melanin, the starting material of the amino acids normally present a tyrosine in the human body[6]. Melanocytes within the tyrosine oxidation by tyrosinase is turned into dopa (3,4-dihydroxyphenylalanine, DOPA, referred to as DOPA) is oxidized DOPA quinone. quinone turns into 5,6-dihydroxy DOPA through auto-oxidation indole and indole-5,6-quinone formation, and finally dark brown melanin are produced. There are a variety of natural chemicals in the human body consisting of the protein. Each chemical, the role of each amino acid or dual granules, ever melanin, melanin mix, etc. that are related to the color black as a raw material, which is formed by the amino acid tyrosine, melanin, type in the amount and distribution of melanin formation under determines the brightness of the hair by a number of factors, such as the degree a person reveals a unique hair color. In other words, it can be decided hair color as black, red, blond according to the type and size of granules of melanin. Black and brown hair color is made with two types of melanin that eumelanin or tyrosine as the most common and most dark pigment. Pheomelanin is noticeable as the color of pale vellow blond. Indicated by red hair, the color

of the red pigment and black pigment, blonde hair color is the result of a mixture of red pigment and yellow pigment. By mixing sand light brown hair, red, brown, and black pigment, the pigment appears black pigment and dark brown hair has lots of black pigment more than the sand light brown hair. The grey hair doesn't have black pigment in the cortex[7-9]. Melanin gives color to the hair as a protein that does not dissolve in water[10]. Tyrosine, an amino acid that is generated by the dermal papilla of melanin prepared as a self-indulgence (0.8~1.8µm long diameter, short diameter 0.3~0.4µm). White hair is state that stop the keratin immigration with black pigment as the oxidation of DOPA quinone did not occur, because it does not make as tyrosinase enzyme. Phenomenon caused by stopping melanin production in melanocytes white hair appears more clearly in the path-way, especially with dark-brown hair of some sort of aging. Dopa quinone, the reaction proceeds in two paths. Cysteine in combination with keratin proteins that exist in and through DOPA chrome path to produce black-brow eumelanin and dopa quinone path to produce a reddish-brown pheomelanin. Thus, the oxidation of the hair dye hair polymerization reaction is an example of a combined response. Reaction and oxidative polymerization of aromatic amines and phenolic monomers combined with the amino acid residues of hair[10]. Against pheomlanin is relatively large in size and can easily be destroyed by chemical, eumelanin is relatively small in size and stable with chemical[11]. The hair of lots of cysteine have lots of pheomelanin, which your hair looks a little red with H2O2, because eumelanin was destroyed first. The study is underway to industrialization path and recently attracted attention as the precursor for the formation of melanin, the stage of 5,6-dihydroxy indole[12]. 5,6-dihydroxyindole was made through synthetic and biological process. Recently bio-process was took notice in hair dve

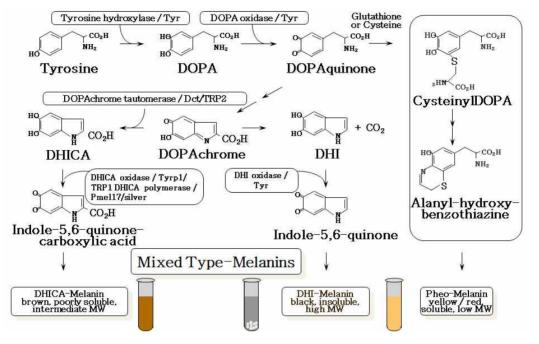


Fig. 1. Pathway to melanin synthesis.

study[13]. Therefore, against their unstable characteristics in the normal air condition, it was quickly brownish color by oxidation[14,15].

In this study, we try to find the stabilizing process of the 5,6-dihydorxyindole using several kinds of coating process. Coating of unstable material with oxidation were very useful technology for stabilizing materials. We try to get know what is the suitable method for stabilizing method through to compare with wet-coating and dry coating method.

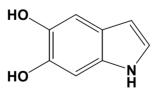


Fig. 2. Scheme of 5,6-dihydroxyindole.

2. Experiments

2.1 Materials

Coating materials used were dimethicon(KF-96-100CS, Shinetsu, Japan), cyclomethicone (TSF405, Momentive, Japan), shea butter(Butirosom pakii, gustav, Brazil), cetyl ethylhexanoate(CEH, BASF, German), dextrin palmitate and used antioxidant material was vitamin E acetate.

2.2 Method

2.2.1 Wet-process

Dimethicone, cyclomethicone and 5,6-dihydroxyindole were mixed well by introducing the coating material. Completely mix, sample was heated to dry at approximately 58°C with the hot air.

	Dimethicone	Cyclomethicone	5, 6-dihydroxyindole
Sample 1	10%	10%	80%

	Dimethicone	Shea butter	CEH	Dextrin palmitate	Vitamin E acetate	5,6-dihydroxyindole
Sample 2	10.0%	-	-	_	-	90.0%
Sample 3		7.0%	5.0%	_	-	88.0%
Sample 4		_	10.0%	1.0%	-	89.0%
Sample 5		_	9.5%	1.5%	-	89.0%
Sample 6		_	9.0%	1.5%	0.5%	89.0%
Sample 7		-	7.5%	3.0%	0.5%	89.0%

Table 2. Composition of Coating Materials in Dry-process

2.2.2 Dry-process

Coating material to solidify at room temperature and melts well when applied to the skin temperature near $36\sim37^{\circ}$ C and is similar to melt composition was composed. As shown in Fig. 3 5,6-dihydroxyindole to distribute the coating material at 40°C and gradually commit. The grinder is a slow

1000rpm rotation. Once the coating dispersion and the oxidation stability of light and air to observe the light/dark, open/closed conditions were approximately 11 days.

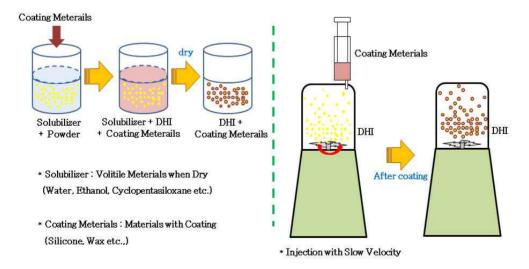


Fig. 3. Scheme of coating process(wet and dry process).

3. Results & Discussion

3.1. Wet-process

Wet-process was not appropriate, 5,6-dihydroxyindole was turned totally black during heat process on 58°C to dry. It is mean already the polymerization reaction was completed and turned melanin. Wet process was not suitable as a coating was investigated.

3.2 Dry-process

Sample 2 of the samples coated with dimethicone. As shown in Fig. 5, dimeticone coated 5,6–dihydroxyindole was the color black appears compared to uncoated sample. This is not oxidization of 5,6–dihydroxyindole, is cause of looking black by wetted dimethicone.

After 2 days open/closed states observed as shown in the Fig. 6. That was exposed to light, there was little difference between the unexposed. Fig. 6 of the photo open photo to the right of each exposed to the O2 proves that was darker side, the influence of light being more affected than that of oxygen that is investigated.

After 8 days samples observed as shown in the Fig. 7. In uncoated samples, the light and open states sample is more dark than unexposed samples with light and air. And in coated samples, there were no effect of light. Therefore, unexposed with air sample was letter dark than exposed sample. This is mean that oxygen is more influence than light.



Fig. 4. Picture of wet-process coating.

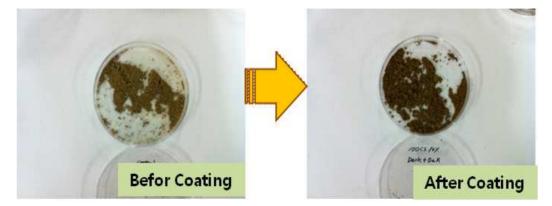


Fig. 5. Picture of sample 2-dihydroxyindole with dimethicone coating.



Fig. 6. Two day after of sample 2 compare with open/closed and light/dark conditions.



Fig. 7. Eight day after of sample 2 compare with open/closed and light/dark conditions.



Fig. 8. Picture of sample 3. 5,6-dihydroxyindole with shea butter and cethylethylhexanoate coating.

In sample 3 cases, shea butter coated samples were brownish, it was not color change but, it was the effects of shea butter more slightly pale than dimethicone coated sample was able to confirm that.

After three days could observed that the color was almost black in all conditions, six days after the polymerization is complete, remarkably melanin could observed that. Shea butter had little effect, but it was not enough the amount of shea butter to coat 5,6-dihydroxyindole all the surface.

In the sample 4 case, dextrin palmitate coated sample had same color with shea butter coated sample 3 case.

After three days of exposure to light, the color difference was less. The difference between open and closed state great. The effect of oxygen is high, and the effect of the light was low.

After 6 days when compared with shea butter coated less discoloration was able to

Sample 3	0 day	3 days	6 days	
Control				
Light + Open	AND	The same Sciences Sciences	A series and the series of the	
Light + Close	Nice Astrony Libert and Libert and	His here (Sea tria) (Sea tria)	Hen here (read tri)	
Dark + Open	An edge Construction	Ha haye (a. +1.0)	Jana Langer (an Enger (an F-d)	
Dark + Close	A MARKAN AND AND AND AND AND AND AND AND AND A	An and An an an an An an an An an an An an an An an an An an an an An an an An an an An an an An an an an An an an an An an an an An an an an an an an An an an an An an an an An an an an an An an an an an An an an An an an An an an An an an an An an an An an an an An an an An an an an An an an an An an an an An an an An an an An an an An an an an an An an	Line for the for the for	

Fig. 9. Change color of sample 3 compared with open/closed and light/dark conditions as days.

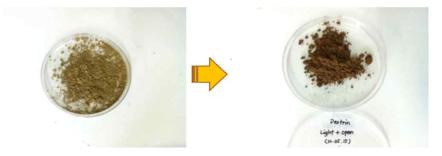


Fig. 10. Picture of sample 4 5,6-dihydroxyindole with dextrin palmitate and cethylethyl hexanoate coating.

Sample 4	0 day	3 days	6 days	
Control				
Light + Open	And Total	Pinta Birthan Birthan Birthan	Janes Banes Contrat	
Light + Close	Internet and a second s	Refe Hitter (Jung g)	Lever Berter Boot #2	
Dark + Open	Arrise Relative Description	Damp Barro	Defin Ark and	
Dark + Close	Denne Bekritag Storig	Peliji Beliji Gwr.27	Anne Bergerater Bergerater Bergerater	

Fig. 11. Change color of sample 4 compared with open/closed and`light/dark conditions as a days.

observe in Fig. 11. After 6 days when compared with shea butter coating discoloration could be less sure. This mean dextrin coating have got a stability against color change with light, and also have got a stability against oxidation with air compare with other coating materials.

In the cases of sample 5, 6, 7 which are to determine the influence that the amount of dextrin palmitate and the vitamin E acetate, after two days in the color difference was not significant of the all samples. Vitamin E acetate and dextrin plamitate almost no difference in the amount of seven days, but all samples were exposed to the light conditions in the open and closed conditions were clear differences in the samples containing of the dextrin palmitate contributes to the stabilization of the 5,6-dihydroxyindole was found to be.

		0 day	2 days	7 days
Light + Open	Sample5			
	Sample6	And the second s		And the second s
	Sample7	And the second s		A REAL PROPERTY AND A REAL
Light + Close	sample5	A STATE	En el Brezel	
	Sample6	A STATE	Arrist Barrier	
	Sample7	A MARKET AND A MAR		A REAL PROPERTY OF THE PROPERT

Fig. 12. Change color of sample 5,6,7 compared with open/closed and light/dark conditions as days.

4. Conclusion

In this study, there is the potential to charge a natural dye 5,6-dihydroxyindole to improve the oxidative stability of the proposed method was dry-coating, coating material dimethicone, shea butter, dextrin palmitae present in the air, the light and the stability of visually evaluated. As a result, the stability on the following materials have suggested.

1. Wet-coating process during drying due to

the oxidation of 5,6-dihydroxyindole was inadequate, dry-coating process was stable.

- 2. Shea butter did not show antioxidant effect.
- 3. Dextrin palmitate oxidation by light and air, showed the effect of preventing this time there was no significant amount.
- 4. Dextrin palmitate vitamin E acetate under conditions of light and heat there was no significant effect in preventing oxidation.

As a stabilizer of the 5,6-dihydroxyindole, dextrin palmitae is expected to get a long-term stable way and dextrin palmitate coated 5,6-dihydroxyindole is expected to stable and efficient coloring agent as a natural hair dye.

REFERENCES

- M. Cichorek, M. Wachulska, A. Stasiewicz, A. Tyminska, "Skin melanocytes : Biology and development", Postepy Dermatologiii Alergologii, **30**, 30 (2013).
- M. Balandrin, M. F., J. A. Klocke, E. S. Wurtele, and W. H. Bollonger, "Natural plant chemicals: Sources of industrial and medicinal materials", Science, **228**, 1154 (1985).
- L. Warwick, L. Morison, "What Is the Function of Melanin?", *Arch Dermatol.* 121(9), 1160–1163 (1985).
- C. J. Vavricka, B. M. Christensen, J. Li, "Melanization in living organisms: A perspective of species evolution", *J. of Protein and Cell*, 1(9), 830 (2010).
- N, Saino, M. Romano, "Viability Is Associated with Melanin–Based Coloration in the Barn Swallow (Hirundo rustica)", *PLoS ONE*, 4(4), e60426 (2013).
- R. P. Shingh, S. sharad, S. Kapur. "Free Radicals and Oxidative Stress in Neurodegenerative Diseases : Relevance of Dietary Antioxidants", *JIACM*, 5(3), 218–25 (2004).

- 7. S. Commo, O. Gaillard, B. A. Bernard, "Human hair greying is linked to a specific depletion of hair follicle melanocytes affecting both the bulb and the outer root sheath", *British J. of Dermatology*, **150**(3), 435 (2004).
- 8. H. M. Bolt, K. Golka, "The debate on carcinogenicity of permanent hair dyes: New insights", *Crit. Rev. Toxicol.*, **37**(6), 521 (2007).
- E. K. Nishimura, *etal.*, "Mechanisms of hair graying: Incomplete melanocyte stem cell maintenance in the niche", *Science*, **5710**, 720–4 (2005).
- S. Kobayashi, H. Higashimura, "Oxidative polymerization of phenols revisited", *Prog. Polym. Sci.* 28. 1015–48 (2003).
- S. Ito, K. Fujita, "Microanalysis of eumelanin and pheomelanin in hair and melanomas by chemical degradation and liquid chromatography", *Anal. Biochem.*, 144(2), 527–36 (1985).
- C. R. Borges, J. C. Roberts, D. G. Wilkins, D. E. Rollins, "Relationship of Melanin Degradation Products to Actual Melanin Content: Application to Human Hair", *Anal. Biochemistry*, **290**, 116–25 (2001).
- Mu-Ill Lim, Dilip G. Patil1, "Mushroom tyrosinase as an oxidant for the synthesis of 5,6-dihydroxyindole derivatives", *Tetrahedron Lett.*,28(33), 3775-8 (1987)
- 14. L. Novellino, M. d'Ischia, G. Prota, "Nitric oxide-induced oxidation of 5.6dihydroxyindole and 5,6-dihydroxyindole -2-carboxylic acid under aerobic conditions: non-enzymatic route to melanin pigments of potential relevance to skin (photo)protection", Biochim Biophys Acta, 1425, 27-35 (1998).
- 15. J. J. Le Minez, B Schmitt. Wet-on-wet coating process, US Patent 4,375,498, (1983).