碳化台灣二葉松落葉製造黑紙之研究

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【摘要】乾旱季節的南台灣原始台灣二葉松富含油脂及樹脂落葉，經久不易分解，易引起森林火災。將二葉松落葉自林地移走，實有所難。利用裝在小卡車上之乾餾設備，運至二葉松林地，就地利用部份落葉當燃料乾餾（420℃、2 hr）二葉松葉，除可得餾出液外，尚可就殘留碳化針葉，磨成細碳粉（通過 200 網目），供作黑紙之黑色料。經本試驗所製得之基重 100g / m^2 黑紙顏色 CIELAB 値分別爲 29／0.33／-1.81，光澤度（75°）36.3% 足可比美含工業用黑碳粉黑紙之顏色。
【關鍵詞】黑紙、碳粉、染料、台灣二葉松、白水

The Manufacture of Black Paper from the Carbonized Fallen Leaves of Taiwan Red Pine

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【Abstract】Over the past years, Taiwan foresters have looked at the damages caused by the forest fires partly came from the oil and resin containing fallen pine leaves in southern Taiwan in dry season. Removal of the fallen leaves of Taiwan Red Pine (*Pinus taiwanensis Hayata*) from forest is impractical and not economic, so it seems feasible to transport a semi-closed drying kiln by truck to the forest site to incinerate the fallen leaves in situ. Besides the distillate collected from the leaves of red pine's dry distillation at 420°C for 2 hours in semi-closed dry kiln, the residual - carbonized pine leaf (abbreviated as pine carbon) - can be ground to carbon powder (pass 200-mesh screen) in a grinder. In view of the color (expressed as CIE $L^*a^*b^*$: 29/0.33/-1.81and BL^* : 31.14) and gloss : 36.3% for a 6% carbon black and Direct Black 38 of 6% added black paper and dyestuff loss in white water during sheet forming, the pine carbon containing black paper (100 g /m^2) is comparable to that of commercial carbon filled black paper.
【Key words】Black paper, carbon powder, dyestuff, Taiwan red pine, white water.

I. Introduction

To prevent forest fire in Taiwan becomes a critical issue due to the increasing global warming effect recently. According to the report of Taiwan Forestry Bureau (Tien, 2001), forest fire has caused great damage about US$ 650,000

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in 2000. In addition, due to the fallen leaves of pine trees are not easy to decay for their abundant oil and resin contents, so forest fires often occur during the dry season i.e., November to March in Taiwan.

To remove the fallen leaves from the forest is apparently impractical and not economic due to most of the forest are in the mountains of Taiwan. How to reduce the occurrence of forest fire in Taiwan? The aim of this study is to incinerate the fallen pine leaves in a semi-closed dry kiln near forest. And then some cooled extractives i.e., methyl alcohol, acids, acetone and wood tar (Wang, 1994) and carbonized pine leaves can be obtained concurrently. By doing so, we have the following advantages:

1.Useful extractives can be obtained in situ forest.
2.Carbonized pine leaves can be used as fertilizer in forest.
3.Application of ground carbonized pine leaves' powder to industrial uses.

The objective of this study tries to apply the carbon black originated from fallen leaves of Taiwan Red Pine to manufacture a high-grade black paper for wrapping, art and printing usage.

Ⅱ. Experimentals

(Ⅰ) Materials:

Fallen leaves of Taiwan Red Pine were collected from Hui-Sun Experimental Forest, National Chung Hsing University, 65 km away from Taichung. Direct Black 38 dyestuff was supplied by Chung-How chemical company, Taiwan. Aluminum sulfate 16~18 H_2O (Santoku chemical company, Ltd., Japan) was used as dye's fixing agent.

(Ⅱ) Procedures:

The fallen leaves of Taiwan Red Pine were incinerated in a semi-closed dry kiln connecting to a condenser at the top of the lid at 420°C for 2 hours to collect the distillate at the exit of condenser. After dry distillation, remove the carbonized residue to a grinder (Retsch grinder, Zm-100, Germany) for grinding. Sifting the ground powder through a 200-mesh screen to give a fine carbon powder.

Determine the particle size distribution and specific surface area of carbon powders with particle analyzer (BI-XDC, Brookhaven Instruments Corporation, USA).

Pour 5 gm carbon powder into a 100 mL-volumetric cylinder. Transfer the volumetric cylinder to a shaker and fix it firmly. Leave the shaker go up and down 100 times for packing the dry carbon powder densely. Read the volume of the packed carbon in cylinder, Vc. Report the density of the carbon powder as 5/Vc (g/cm^3) .

Put the commercial and pine carbon powders by 6% (on dry pulp) in NBKP and LBKP, refinining the 10%-consistency pulp together with carbon powder in a PFI to 450 mL freeness. Remove the carbon-containing beaten pulps to a beaker and dilute with water to 3% pulp consistency. Add dyestuff (Direct Black 38) of 6% (on dry pulp) to the carbon-containing pulps for thorough mixing. Making 100 g /m^2 paper sheet in a sheet mould in accordance with TAPPI Standard T205 sp-95.

Measure the color (expressed as CIE $L^*a^*b^*$), k/s (Tappi Standard T562 pm-96) and BL^* (Tappi standard, 1994; Kuo, 1998) values with Macbeth Color-eye 3000 , Xenon lamp, measured the reflectance of paper by 20 nm division in the wavelength range of 400 - 700 nm (USA) for the evaluation of the blackness of samples.

Add 2, 4, 6% aluminum sulfate (on dry pulp) to the above stock for determining their potential (mV) with particle charge analyzer (Muteck PCD 03 pH, Switzerland) and understanding its influence on the colorants retention on papers. We also determine the suspending solid (expressed as ppm) in white water by weighing the materials retained on micro-pore filter for each sheet making. The amounts of colorant's loss (expressed as concentration, %) in filtrate are measured with UV spectrophotometer (HITACHI, U-3000, Japan).

An experimental-type of the two-roll calender (top roll: rubber-covered soft roll; bottom: heated stainless hard roll) is shown in Fig. 1. The temperature and nip pressure can be adjusted manually. The incoming paper is transported through the nip.

III. Results and discussion

(Ⅰ) *Morphologies of carbon particles and balck papers*

The increase in paper balckness caused by the addition of carbon is due to the light absorption of carbon and its distribution on paper surface. In a composite structure of black paper, the sizes, shapes and number of carbons on the surface of paper is essential to the shade.

From Fig. 2 and 3 it can be seen that the commercial carbon has needle-like structure that is significantly different from plate-like structure of pine carbon. For more light absorption, however, the effect of particle shape clearly dominates (see Table 2). This study has shown that the carbon retention on fibers can be attained by filling the carbon particles into fiber cell wall or fiber lumen during refining (see Figs. 4, 5). In such cases retention by mechanical entrapment of carbon particle could remain an important mechanism in this study.

The density of pine carbon 0.43 g/cm^3 is higher than that of commercial carbon powder 0.38 g/cm^3. The lower density indicates the bulk structure of commercial carbon particles.

Finely-divided carbon blacks are added to papermaking furnishes to increase the blackness of black papers. The carbon particles serve to fill

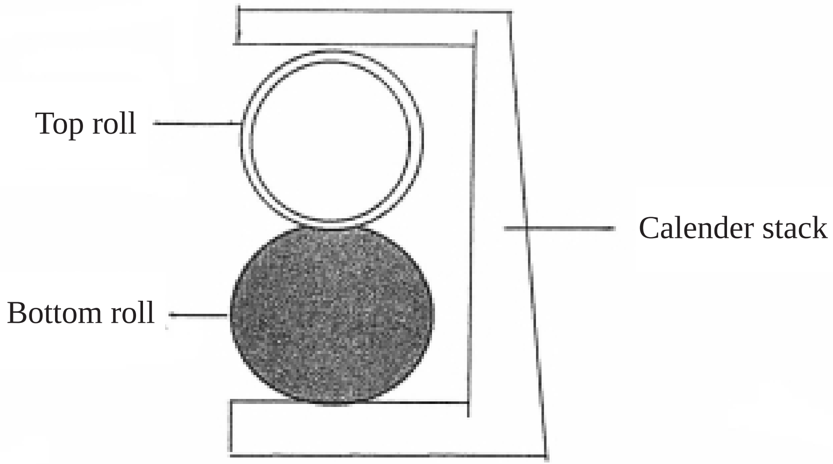

Fig. 1. Top roll and bottom roll of a calender.

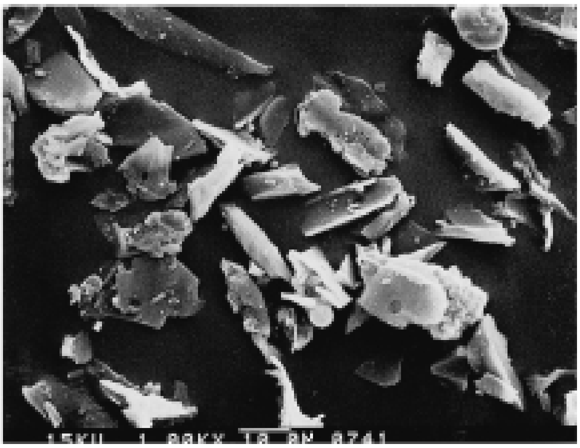

Fig. 2. Industrial carbons have needle-like structure.

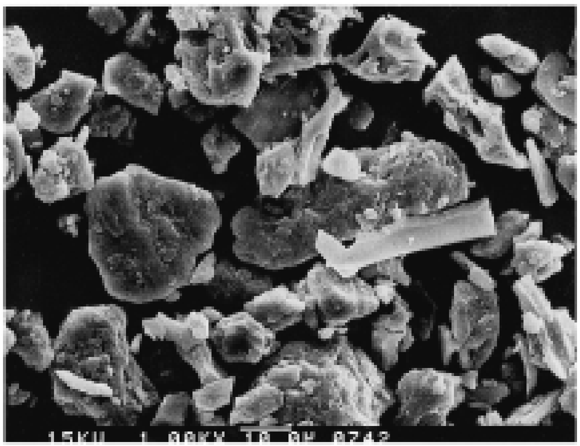

Fig. 3. Taiwan Red Pine leaf carbons have plate-like structure.

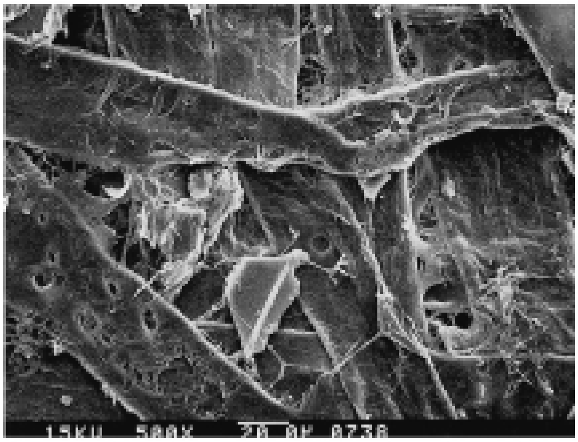

Fig. 4. Scanning electron micrograph of commercial carbon-containing paper.

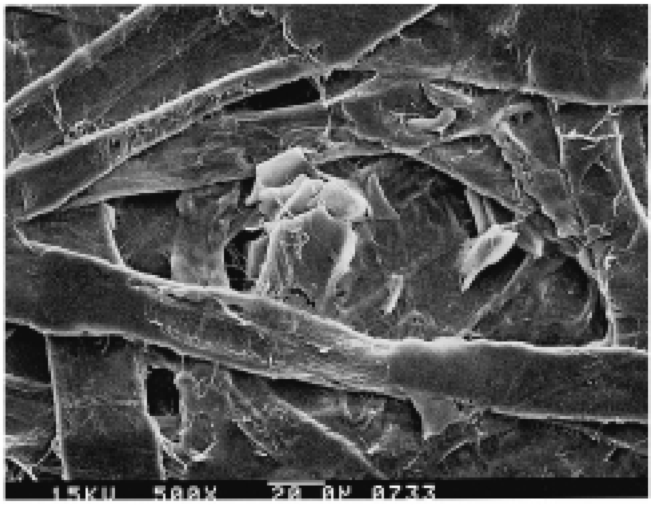

Fig. 5. Scanning electron micrograph of pine carbon-containing paper.

in the spaces and crevices between the fibers (see Fig. 4,5) thus producing a dark and dull black papers. The size and surface area of carbon blacks, in which influence the light absorption, must affect the blackness of black papers. Table 8 shows that the particle size of pine leaf carbons is finer than that of the commercial carbon (0.18 μ m : 6.26 μ m) and also has larger surface area (13.29 m^2/g) , by which can be favorable to increase the light absorption, when compare to commercial carbon (0.375 m^2/g). In other words, pine leaf carbon powder may impart dull shade to the black paper.

(II) *Color of black papers*

As indicated in Table 2, NBKP always has higher coloring strength (lower L^* values) than that of LBKP with the addition of both pine carbon and Direct Black 38 dyestuff. Interestingly saying, pine carbon produced from Taiwan Red Pine Leaves gives dull shade (low lightness (L^*)) for black paper when comparing to commercial carbon.

Black colorant retention on paper is essential to the blackness of black paper. The basic requirements of black colorants retention on paper are as follows (Kuo, 1987):

1.A high opacity and light absorbance of base paper.
2. Good retention of black colorants on paper.
3.Even distribution of retained carbon particles on paper surface.
4.Objective evaluation of blackness and color of black paper.

Usually, a black paper with lower BL^* value (Kuo, 1998) indicated preferred duller shade. As indicated in Table 3, pine carbon containing black papers (L^*:31.17 & 33.37) showed duller shade than those of commercial carbon containing ones (L^*:31.26 & 36.87). It is noted that there is no significant color difference (ΔE = 4.3) between NBKP-PC-DB and LBKP-PC-DB when compared to commercial carbon containing black papers (ΔE = 23.0). In view of k/s (coloring strength), the carbon addition led to the increased k/s (duller shade) for varying 6% direct Black 38 dyed papers.

Table 1. Particle size distribution of various carbon particles.

Specimens	Size distribution,%					Av, μm	Specific surface area m^2/g
Industrial carbon	< 4.75 μm	<4.90 μm	<5.97 μm	<7.54 μm	<8.04 μm		
	10	16	50	84	90	6.26	0.375
Carbon of Taiwan	<0.02 μm	<0.032 μm	<0.1 μm	<0.167 μm	<0.178 μm		
Red Pine leaves	10	16	50	84	90	0.18	13.29

Table 2. The color of various black papers.

Paper specimens	Color (CIELAB)		
(Order of addition)	L*	a*	b*
NBKP-IC[1]-DB[2]	29.12	1.34	-0.80
LBKP-IC-DB	35.03	-0.25	-1.59
NBKP-PC[3]-DB	29.03	0.33	-1.81
LBKP-PC-DB	30.84	0.57	-1.96
NBKP-DB	31.53	0.61	-2.29
LBKP-DB	34.62	-0.40	-2.29

1. IC : industrial carbon
2. DB : Direct Black 38 dyestuff
3. PC : pine carbon

Table 3. BL^*, k/s and color difference of various black papers.

Paper specimen (Order of addition)	BL*	k/s	ΔE
NBKP-IC-DB	31.26	7.65	0.00
LBKP-IC-DB	36.87	5.26	23.00
NBKP-PC-DB	31.17	8.00	0.00
LBKP-PC-DB	33.37	7.03	4.30
NBKP-DB	34.43	6.65	0.00
LBKP-DB	37.31	5.55	9.49

$BL^* = L^* + |a^*| + |b^*|$; k...absorption coefficient, s...scattering coefficient

$k / s = (1 - R\infty)2/2R\infty$ ($R\infty$: minimum reflectance in the wavelength range of 400-700 nm)

$\Delta E = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{0.5}$

(III) *Elemental analysis*

In order to evaluate the distribution of carbonized pine components in carbon and paper sheet, elemental analysis for nitrogen , carbon and hydrogen in leaf were carried out in this experiment. Table 4 showed that little higher nitrogen content (3.63%) in pine carbon might account for the rich nitrogen in fresh pine leaf. In general, no apparent differences for the carbon contents in various black papers. Note that each black paper showing different blackness (Table 2, 3) indicated that the blackness is significantly affected by carbon size, its distribution and affinity to fibers as well.

(IV) *Effect of calendaring on the gloss and color of black papers*

As Table 5 shows, the more number of nips and higher nip pressure applied (Fig. 1.) which result in more compaction on the papers, the higher gloss of black papers. Additionally, the lower gloss of LBKP containing black paper is apparently due to the different properties of

Table 4. Elemental analysis of various carbons and black papers.

Paper specimen	N,%	C,%	H,%
IC	1.87	71.07	2.74
PC	3.63	70.60	6.58
NBKP-IC-DB	1.65	42.04	6.66
LBKP-IC-DB	1.63	44.66	6.85
NBKP-PC-DB	1.40	43.57	6.45
LBKP-PC-DB	1.60	44.49	6.27

Table 5. Effect of calendaring on the gloss of various black papers.

Paper specimen	Gloss,% (75°) Pressure, kgf / cm^2				CIELAB[1]			BL*1
	0.0	1.0 1st nip	2.0 2nd nip	4.0 3rd nip	L*	a*	b*	
NBKP-IC-DB	14.2	27.7	19.8	36.3	29.18 (29.12)[2]	1.23 (1.34)	-0.27 (-0.80)	30.75 (31.26)
LBKP-IC-DB	9.1	18.4	22.8	28.8	31.79 (35.03)	0.79 (-0.25)	-1.16 (-1.56)	33.74 (36.87)
NBKP-PC-DB	7.5	22.6	27.3	33.9	29.37 (29.03)	0.38 (0.33)	-1.01 (-1.81)	30.76 (31.17)
LBKP-PC-DB	5.8	19.3	22.9	28.6	31.10 (30.84)	0.48 (0.57)	-1.18 (-1.96)	32.76 (33.37)

1. All values are for 3rd calendered papers.
2. Numbers in ( ) are for uncalendered papers.

carbons and chemical behavours of fibrillar fibers in NBKP and LBKP respectively at the same freeness (420 mL CSF) of pulps.

The gloss of uncalendered NBKP- PC -DB and LBKP - PC - DB are lower than that of IC containing ones (14.2 / 7.5; 9.1 / 5.8). However, there are apparent increase in gloss of 3rd calendered PC containing black papers (7.5↗33.9; 5.8↗28.6) which were comparable to IC containing papers. The reason may be due to the carbonized leaves' of Taiwan red pine contain lots of resin and oily materials to increase the smoothness of black papers, when the handsheets were compacted with the rolls of calender.

Also note in Table 5, the more nip applied, the more light absorbed by the densified black paper as the lower BL^* values indicated.

(V) *Effect of alum on the color of black paper*

Table 6 indicated that the coloring strengths of pine and industrial carbon powders applied to NBKP with or without the addition of alum were higher than those of the LBKP, i.e., higher k/s and lower BL^* values for the previous ones. By measuring the streaming potential of various stocks has shown that the positive charge of alum attracted some of the negative charge carbon particles onto fiber surface, which led to more carbon retention on pulps and duller shade can be resulted. The quantity of alum required for an isoelectric point to be reached is described as the

Table 6. Effect of alum on the charge of white water and color of black paper.

Pulps	Alum, %	Charge of white water mV	CIE L*a*b*	k/s	BL*
NBKP	0	-384	29.25/-0.73/-2.34	8.20	32.32
+	2	-45	29.42/0.30/-2.28	7.86	32.00
PC	4	-30	29.21/0.92/-0.99	7.75	31.12
	6	-6	27.74/0.97/-1.10	8.64	29.81
LBKP	0	-380	31.80/-1.48/-3.03	7.12	36.31
+	2	-88	34.13/-0.19/-2.37	5.70	36.69
PC	4	-13	31.99/0.02/-1.74	6.53	33.75
	6	-5	31.02/0.07/-1.21	6.96	32.30
NBKP	0	-307	26.81/-0.63/-2.63	9.89	30.07
+	2	-96	30.78/-0.10/-2.41	7.21	33.29
IC	4	10	27.99/0.70/-1.23	8.57	29.92
	6	34	28.78/0.47/-1.03	8.09	30.28
LBKP	0	-380	31.68/-1.79/-3.76	7.35	37.23
+	2	-56	37.05/-1.66/-3.81	5.02	42.52
IC	4	-39	32.19/-0.48/-2.14	6.60	34.81
	6	-26	32.45/-0.21/-1.77	6.37	34.43

Order of addition: pulp + carbon → beating in PFI to 450 mL CSF → 6% Direct Black 38 → 0,2,4,6 % alum added →sheet forming most dullest shade among the black papers. Interestingly, black paper made from NBKP+IC with no alum addition gave lower BL* (30.07, Table 7) when compared to alum-adding ones. The real reason is worthy to be investigated further. Table 7 showed that the dye (Direct Black 38) loss in white water after the removal of suspending carbon particles depended on the amount of alum (as fixation of dyestuff) added. In other words, the more alum added (< 6%), the duller shade of black paper can be made.

(Ⅵ) *Effect of alum addition on the dye loss in effluents*

In order to reduce the dye (Direct Black 38) loss in effluents for the stringent environmental regulations in Taiwan, we added 2-6% alum (as fixing agent) in stock. Table 7 showed that the dye loss (ppm) in white water could be greatly reduced by more cationic alum dosages. In other words, more alum addition can lead to more dye fixing on fibers. Due to too much alum (more acidic) is harmful to the permanence of papers, it seems that the optimum alum level should be less than 2%. By 2% alum level, carbon-added NBKPs has less dye loss than that of the LBKPs.

Finely-divided carbon blacks are added to papermaking furnishes to increase the blackness of black papers. The carbon particles serve to fill in the spaces and crevices between the fibers (see Fig. 4,5), thus producing a dark and dull black

Table 7. Dye (Direct Black 38) loss in white water for making various carbon containing black papers.

Pulps	Dye loss in white water, ppm			
	Alum, %			
	0	2	4	6
NBKP+PC	29.85	4.66	1.54	1.14
LBKP+PC	28.32	17.93	2.54	2.12
NBKP+IC	28.41	3.35	1.63	0.99
LBKP+IC	35.26	16.21	1.44	1.13

1.Filtrates were obtained from the white water drained through a 0.45-μm micro-pore film.
2.Dye loss was calculated as the concentration of dyestuff in filtrate by using of UV spectrophotometer

Table 8. Particle size analysis for various carbon powders.

Specimens	Size distribution,%					Av, μm	Specific surface area m²/g
commercial carbon	< 4.75μm	<4.90μm	<5.97μm	<7.54μm	<8.04μm		
	10	16	50	84	90	6.26	0.375
Carbon of Taiwan Red Pine leaves	<0.02μm	<0.032μm	<0.1μm	<0.167μm	<0.178μm		
	10	16	50	84	90	0.18	13.29

papers. The size and surface area of carbon blacks, which influence the light absorption, must affect the blackness of black papers. Table 8 shows that the particle size of pine leaf carbon is finer than that of the commercial carbon (0.18 μm : 6.26 μm) and also has larger surface area (13.29 m^2/g) , by which can be favorable to increase the light absorption, when compare to commercial carbon (0.375 m^2/g). In other words, pine leaf carbon produced may impart dull shade to the black paper.

Ⅳ. Conclusion

Finely divided carbon powder can be obtained by incineration of fallen leaves of Taiwan Red Pine at 420℃ for 2 hours in a semi-closed dry kiln, and then to ground in a grinder. As expected, CIE $L^*a^*b^*$ = 29.0/0.33/-1.80 and BL^* = 31.41 of 6% dye (Direct Black 38) and 6% pine carbon blended sheet (100 g/m^2) prepared by handsheet mould indicated that the color of pine carbon containing black papers are comparable to those commercial carbon-added ones.

Calendaring pine carbon containing black paper increases its gloss significantly. Adding less than 2% alum in stock can decrease the dye loss in effluents. Due to the low BL* value (< 32.0) of black papers in this study , the carbon powder prepared from Taiwan Red Pine leaf has the potential for the manufacturing of high-grade black paper.

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