リサイクルにおけるパルプ物性変化 —ソーキングの影響—

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Changes of Pulp Properties by Recycling —Effects of Alkaline Soaking—

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Many works concerning to recycling of paper have suggested that the recycling decreases pulp strengths and optical properties. In these studies, the recycling procedure only consists of repeated treatment such as pulping, drying and re-pulping.

However, actual deinking process usually has a soaking process which is carried out with alkaline chemicals such as sodium hydroxide and hydrogen peroxide.

In this paper, we show the significance of the soaking in the deinking process. For hardwood bleached kraft pulp, the soaking with alkaline chemicals affects negative inferences to pulp strengths, however, the soaking with hydrogen peroxide affects positive inferences. On the other hand, the soaking has a little influence on the TMP properties except optical properties.

Keywords : Recycling, Deinking, Alkaline chemicals, Hydrogen peroxide, Alkaline soaking

分類 : G₅ 脱インキ, R₅ 古紙パルプ

1. 緒 言

近年においては環境に対する意識の高まりから、リサイクル対応商品への需要が強く、新たな古紙配合製品の開発や、古紙配合率の増加が要求されている。それに伴い、古紙のリサイクルは一層推進されるが、その一方で高品質紙には、バージンパルプと同等の品質が要求される。このため、リサイクルによるパルプ物性の変化を把握しておくことが必要である。

数年前まで、リサイクルに適した木材選定や、リサイクルによる物性変化を調査するために、チップや古紙のリサイクル試験・研究が盛んに行われてきた。リサイクルテストに関しては、離解した古紙から手抄シートを作り、それを乾燥させて紙とした後、また再離解して再び手抄シート

を作製するといった方法で、薬品処理を行わずにパルプ物性の変化を調査した報告が主であった。また、これらのパルプ強度の報告では、同一緊度での比較がほとんどされていなかった^{1)~7)}。

しかし、実際の中紙処理プロセスでは、原料とする古紙と同等、もしくはそれ以上の品質への再生を要求されることが多く、そのため苛性ソーダなどアルカリ性薬品で脱インキ処理（アルカリソーキング）を行っている。更に、元のパルプより白色度の高いパルプが要求される場合には、アルカリ性下で、過酸化水素による漂白処理を行っている。

アルカリ性薬品や過酸化水素によるパルプへの影響は、パルプの膨潤や繊維間結合の増加などが感覚的に推測されているものの、これらの薬品の影響は、単に TMP や CTMP 製造時における影響を調査したものであるか^{8)~15)}、リサイクル性の調査であっても、各々の薬品を一定量添加して処理した場合のものや^{16), 17)}、離解処理のみでソーキン

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グ（アルカリ過酸化水素漂白）処理を行っていないものであった¹⁸⁾。LBKPまたはTMPを抄紙・熱乾燥したものを出発原料として、各々の薬品添加率を変化させてソーキング処理を行った場合のパルプ物性の挙動を検討した報告例はない。そこで本研究では、アルカリ性薬品による脱インキ処理を考慮し、単に湿潤・乾燥を繰り返したりサイクルテストではなく、より実際的な古紙処理に即した薬品添加条件下で古紙リサイクル試験を行い、同一緊度におけるパルプの物性変化を評価した。

2. 実験

一般的には、一度抄紙され、乾燥（熱履歴）工程を経たパルプは角質化し、繊維間結合も減少すると考えられるが、国内における洋紙系のDIP処理工程では、通常脱インキ工程としてソーキング（アルカリ過酸化水素漂白）処理を含む場合が主である。ソーキングにおける薬品添加率は、原料古紙や目標品質（製品品質）によって大きく異なるが、一般的には苛性ソーダが対パルプ0.5～3.0%、珪酸ソーダが1.0～5.0%、脱墨剤が0.01～0.5%、過酸化水素が0.2～3.0%である。リサイクルにおけるパルプの物性変化は、ソーキング処理工程の有無によって大きく異なることが予想される。そこで、ソーキング処理において、脱インキ薬品として用いられているアルカリの添加率や、アルカリ焼け防止剤、あるいは漂白剤として用いられている過酸化水素の添加率を変動させてパルプ物性に与える影響について検討を行った。

2.1 概要

1) まず、使用した原料パルプと、これから調製した手

【HBKP (hardwood bleached kraft pulp)】

Fig. 1 Preparation and characterization of Starting materials (HBKP)

【TMP】

Fig. 2 Preparation and characterization of Starting materials (TMP)

Table 1 Pulp and sheet properties (HBKP)
Effects of drying, repulping, and soaking without alkaline or H₂O₂

	a	b	c	d
	never dried pulp	sheet forming, heat drying and repulping	+soaking treatment (only for 1.8% H ₂ O ₂ applied)	+soaking treatment (only for 3.6% alkaline applied)
Fiber length (mm)	0.605	0.615	0.595	0.585
Fines (%)	0.68	0.57	0.59	0.61
Cell wall thickness (μm)	5.3	4.7	4.8	4.6
CSF (ml)	450	470	480	515
A fixed pressure (3.5 kg/cm ²)				
Sheet density (g/cm ³)	0.671	0.576	0.584	0.552
A fixed sheet density (g/cm ³)	0.6			
Tear index (mN·m ² /g)	8.5	7.1	7.8	6.0
Tensile index (N·m/g)	58	37	43	37
Opacity (%)	77.2	81.7	79.4	80.9
Scattering coefficient (cm ² /g)	365	454	430	443
ISO Brightness (%)	82.5	83.4	87.3	84.2

Table 2 Pulp and sheet properties (TMP)
Effects of drying, repulping, and soaking without alkaline or H₂O₂

	a	b	c	d
	never dried pulp	sheet forming, heat drying and repulping	+soaking treatment (only for 1.8% H ₂ O ₂ applied)	+soaking treatment (only for 3.6% alkaline applied)
Fiber length (mm)	1.545	1.525	1.470	1.390
Fines (%)	1.26	1.13	1.26	1.49
Cell wall thickness (μm)	8.7	8.9	8.6	8.9
CSF (ml)	90	105	145	170
A fixed pressure (3.5 kg/cm ²)				
Sheet density (g/cm ³)	0.386	0.398	0.358	0.389
A fixed sheet density (g/cm ³)	0.4			
Tear index (mN·m ² /g)	7.3	7.9	7.2	7.7
Tensile index (N·m/g)	38	42	38	38
Opacity (%)	97.5	97.2	94.4	97.1
Scattering coefficient (cm ² /g)	597	553	555	528
ISO Brightness (%)	52.9	52.1	58.9	47.7

抄シートの特性を調べた。その手順を Fig.1, Fig.2 に、また、原料パルプとシートの特性を Table 1(a), Table 2 (a) に示す。次いでこのシートを熱乾燥した後、再離解したパルプ及びこのパルプで作成したシートの特性を調べた。抄紙・熱乾燥・再離解後のパルプとシートの特性を Table 1 (b), Table 2 (b) に示す。

2) 次いで、アルカリソーキングにおけるアルカリ添加率の影響を調べるため、原料パルプより抄紙・熱乾燥・再離解後のパルプを出発原料とし、これに過酸化水素一定量添加条件下で、アルカリを様々な添加率で加えてソーキングを行い、得られたパルプと作成したシートの特性を調べた。

3) 同様にして、過酸化水素添加率の影響を調べるため、アルカリ添加率を一定として、過酸化水素を様々な添加率で加えてソーキングを行い、得られたパルプと作成したシートの特性を調べた。

実験方法の概略をまとめて Fig.3 に示す。

2.2 様々なアルカリ添加率におけるソーキング処理

工場実機製造 LBKP (*Eucalyptus globules/Acacia auriculi-formis*, 450 ml CSF, 82.5% ISO) 及び TMP (*Picea jezoensis/Abies sachalinensis/Picea glauca*, 90 ml CSF, 52.9% ISO) を脱水し、これらのパルプに Fig.1, Fig.2 記載の処理を行うことにより、原料パルプとした。これらのパルプを用いて、抄紙・熱乾燥したシートを下記テストの出発原料として用いた。

これらの出発原料を使用し、Fig.3 記載の手順に従って

ソーキング実験を行った。まず試験用パルパーを用い、苛性ソーダを純分換算で対パルプ 0.4% 添加して、パルプ濃度 2% で 20 分間離解を行った。なお、薬品添加率は、以降純分換算で表記する。

次にパルプ濃度 35% に脱水し、苛性ソーダ、珪酸ソーダを添加して攪拌した後、過酸化水素を添加し、パルプ濃度 25% に調製して、60℃ で 2.5 時間、恒温槽でソーキング（アルカリ過酸化水素漂白）処理を行った。この際、過酸化水素は対パルプ 1.8% 一定で添加し、苛性ソーダと珪酸ソーダは、トータルアルカリ (as NaOH として計算：珪酸ソーダは純分換算値に 0.331 を乗じた数値) として対パルプ 0~3.6% (苛性ソーダ/珪酸ソーダ比率 = 70/30 (as NaOH)) の濃度比率の範囲に変化させて添加した。ソーキング処理後はパルプ濃度 1.5% に希釈し、試験用パルパーで 2 分間離解を行った。続いて、硫酸を添加して再び試験用パルパーで 1 分間離解を行い、pH を中性に調整した後、パルプ特性を測定した。また、これらのパルプを用いて一定の坪量にて手抄を行い、規定圧力 (3.5 kg/cm²) にてプレス処理をし、風乾させてシートを作製した (JIS P 8222 参照)。同一坪量に手抄したシートは、ソーキング処理や薬品添加率によって緊度が異なるため、紙力測定に用いるシートは、手抄後の湿紙プレスの圧力を変化させ、緊度の変化と各パラメーター値から得られるグラフから、同一緊度での各パラメーター値を内挿値で求めた。

作製したシートは、紙力試験として、引裂き強度 (JIS P 8116)、破裂強度 (JIS P 8113)、耐折強度 (JIS P 8112)

Fig. 3 Flow chart of test method

を評価した。光学特性は、白色度 (JIS P 8148), 不透明度・比散乱係数 (JIS P 8149) を測定し, 評価した。また, 繊維長・ファイン量・繊維壁厚は KAJAANI Fiber Lab で測定した (JIS P 8226)。

2.3 様々な過酸化水素添加率におけるソーキング処理

Fig. 1, Fig. 2 記載の出発原料 (手抄シート) を用い, Fig. 3 記載の手順に従って離解・脱水後, ソーキング (アルカリ過酸化水素漂白) 処理を行った。この際, トータルアルカリ (as NaOH) は対パルプ 3.6% (苛性ソーダ/珪酸ソーダ比率=70/30: 苛性ソーダ 2.5%/珪酸ソーダ 3.3% (as NaOH で 1.1%) 一定で添加して攪拌した後, 過酸化水素 0~1.8% の範囲で変化させて添加した。この他は, 2.2 と同様な処理を行い, パルプ特性の測定, 紙力試験用シートの作製, シート特性の評価を行った。

3. 結果および考察

3.1 ソーキング処理におけるアルカリ添加率の影響

ソーキング処理において, 過酸化水素を一定添加 (対パルプ 1.8%) で固定し, アルカリの添加率を変動させてパルプ物性に与える影響について検討を行った。パルプ物性, シート物性の一覧を Table 3, Table 4 に示す。また, アルカリ添加なし (過酸化水素 1.8% のみ) の結果を, 比較

のために Table 1 (c), Table 2 (c) に示す。

3.1.1 パルプ物性, シート緊度

1) LBKP

フリーネス 450 ml に調整した未乾燥の工場実機製造 LBKP, これを抄紙・熱乾燥・再離解したパルプ, 更に, 再離解後にソーキング工程として過酸化水素 (対パルプ 1.8%) のみ添加の温浴処理 (終 pH 5.1) を行ったパルプ, それぞれについて, パルプ特性, 及びそのパルプを用いて作製したシートのシート緊度を Table 1 に示す。未乾燥の LBKP (Table 1 (a)) と比較した場合, 抄紙・熱乾燥・再離解した後のパルプ (Table 1 (b)) のフリーネスは増加 (450→470 ml) し, ファイン分と (0.68→0.57%) 繊維壁厚は低下 (5.3→4.7 μm) した。このパルプで作製したシートは, 未乾燥の LBKP で作成したシートと比較して緊度が大幅に低下 (0.671→0.576 g/cm^3) した。しかし, 離解後に過酸化水素のみ添加のソーキング処理を行った場合 (Table 1 (c)), ソーキング未処理に比べてフリーネスは増加 (470→480 ml) し, このパルプで作製したシートの緊度は若干増加 (0.576→0.584 g/cm^3) した。

ソーキング処理時のアルカリ添加率を増加 (終 pH 11.1~11.7) した場合, パルプのフリーネス (Fig. 4), 緊度 (Fig. 5) はほとんど変化が認められなかった。

Table 3 Pulp and sheet properties (HBKP)

Effects of alkaline peroxide treatment on the pulp and sheet properties at a different alkaline charge

Alkaline charge (%)	0	1.8	2.7	3.6
Peroxide charge (%)	1.8			
Fiber length (mm)	0.595	0.595	0.585	0.595
Fines (%)	0.59	0.66	0.72	0.57
Cell wall thickness (μm)	4.8	4.6	4.8	4.6
CSF (ml)	480	475	480	470
A fixed pressure (3.5 kg/cm ²)				
Sheet density (g/cm ³)	0.584	0.579	0.597	0.593
A fixed sheet density (g/cm ³)	0.6			
Tear index (mN·m ² /g)	7.8	6.7	7.0	6.4
Tensile index (N·m/g)	43	42	40	41
Opacity (%)	79.4	78.8	78.6	78.1
Scattering coefficient (cm ² /g)	430	431	429	416
ISO Brightness (%)	87.3	90.0	90.0	89.9

Table 4 Pulp and sheet properties (TMP)

Effects of alkaline peroxide treatment on the pulp and sheet properties at a different alkaline charge

Alkaline charge (%)	0	1.35	1.8	2.7	3.6
Peroxide charge (%)	1.8				
Fiber length (mm)	1.470	1.455	1.435	1.390	1.440
Fines (%)	1.26	1.32	1.38	1.51	1.40
Cell wall thickness (μm)	8.6	8.7	9.0	8.9	9.2
CSF (ml)	145	160	165	150	145
A fixed pressure (3.5 kg/cm ²)					
Sheet density (g/cm ³)	0.358	0.359	0.368	0.388	0.394
A fixed sheet density (g/cm ³)	0.4				
Tear index (mN·m ² /g)	7.2	8.1	7.9	7.8	7.6
Tensile index (N·m/g)	38	38	38	38	39
Opacity (%)	94.4	91.7	91.2	91.4	91.4
Scattering coefficient (cm ² /g)	555	557	549	566	558
ISO Brightness (%)	58.9	66.4	67.3	67.6	66.9

2) TMP

TMP は、LBKP と異なる挙動を示した。レーテンシー除去後の未乾燥の工場実機製造 TMP、これを抄紙・熱乾燥・再離解したパルプ、更に再離解後にソーキング工程として、過酸化水素のみ添加の温浴処理（終 pH 4.9）を行ったパルプ、それぞれについて、パルプ特性、及びそのパ

ルプを用いて作製したシートの緊度を Table 2 に示す。抄紙・熱乾燥・再離解した後のパルプ（Table 2 (b)）は、未乾燥の TMP（Table 2 (a)）と比較した場合、フリーネスは増加（90→105 ml）し、ファイン分は低下（1.26→1.13%）したが、繊維壁厚はほぼ同等（8.7→8.9 μm ）であった。このパルプで作製したシートは、未乾燥の TMP

Fig. 4 Effects of alkaline peroxide treatment on the C.S.F. at a different alkaline charge

Fig. 6 Effects of alkaline peroxide treatment on the tear index at a different alkaline charge

Fig. 5 Effects of alkaline peroxide treatment on the sheet density at a different alkaline charge

Fig. 7 Effects of alkaline peroxide treatment on the tensile index at a different alkaline charge

で作成したシートと比較して緊度が若干増加 ($0.386 \rightarrow 0.398 \text{ g/cm}^3$) した (Table 2 (b))。しかし、離解後に過酸化水素のみ添加のソーキング処理を行った場合 (Table 2 (c))、ソーキング未処理に比べてフリーネスは増加 ($105 \rightarrow 145 \text{ ml}$) したにもかかわらず、ファイン分も増加 ($1.13 \rightarrow 1.26\%$)、繊維壁厚はほぼ同等 ($8.9 \rightarrow 8.6 \mu\text{m}$) であった。このパルプで作製したシートの緊度は大幅に低下 ($0.398 \rightarrow 0.358 \text{ g/cm}^3$) した (Table 2 (c))。

ソーキング処理時にアルカリを添加した場合、対パルプ 2% 未満の添加率 (終 pH 8 未満) ではパルプのフリーネスは増加し (Fig. 5)、緊度の増加はわずかであるが、アルカリ添加率が 2% を超える (終 pH 8 以上) と、アルカリ添加率が増加すると共にフリーネスは減少する傾向にあり (Fig. 5)、緊度も顕著に増加した (Fig. 4)。

3.1.2 シート特性

1) LBKP

作製したシート特性を、2.2 に示した様に、同一緊度で比較した。抄紙・熱乾燥・再離解を行ったパルプで作製した LBKP のシート (Table 1 (b)) は、未乾燥の LBKP を用いて作成したシート (Table 1 (a)) に比べて比引裂強さは低下 ($8.5 \rightarrow 7.1 \text{ mN.m}^2/\text{g}$) し、比引張強さも低下 ($58 \rightarrow 37 \text{ N.m/g}$) した。しかし、再離解後に過酸化水素のみ

添加のソーキング処理を行うことで (Table 1 (c))、ソーキング未処理に比べて比引裂強さは向上 ($7.1 \rightarrow 7.8 \text{ mN.m}^2/\text{g}$) し、比引張強さも向上 ($37 \rightarrow 43 \text{ N.m/g}$) した。ところが、ソーキング処理時のアルカリ添加率が増加するに従い、比引裂強さ (Fig. 6) は大幅に低下し、比引張強さ (Fig. 7) も低下傾向を示した。

2) TMP

抄紙・熱乾燥・再離解を行ったパルプで作製した TMP のシート (Table 2 (b)) は、未乾燥の TMP を用いて作成したシート (Table 2 (a)) に比べて、LBKP の場合とは逆に比引裂強さは向上 ($7.3 \rightarrow 7.9 \text{ mN.m}^2/\text{g}$) し、比引張強さも向上 ($38 \rightarrow 42 \text{ N.m/g}$) した。しかし、再離解後に過酸化水素のみ添加のソーキング処理を行った場合 (Table 2 (c))、ソーキング未処理に比べて比引裂強さは低下 ($7.9 \rightarrow 7.2 \text{ mN.m}^2/\text{g}$) し、比引張強さも低下 ($42 \rightarrow 38 \text{ N.m/g}$) した。また、ソーキング処理時にアルカリを添加した場合、対パルプ 2% 未満の添加率では比引裂強さは向上したが (Fig. 6)、添加率が 2% を超えると、アルカリ添加率が増加するに従い低下傾向を示した。また、比引張り強さは、ソーキング処理時にアルカリを添加した場合、対パルプ 2% 未満の添加率では変化が認められないが (Fig. 7)、アルカリ添加率が 2% を超えると、若干向上傾向を示し

Fig. 8 Effects of alkaline peroxide treatment on the opacity at a different alkaline charge

Fig. 9 Effects of alkaline peroxide treatment on the scattering coefficient at a different alkaline charge

た。

3.1.3 光学特性

1) LBKP

同一緊度で比較した場合、LBKP はソーキング処理工程として過酸化水素のみ添加のソーキング処理を行うことで (Table 1 (c)), ソーキング未処理 (Table 1 (b)) に比べ、不透明度が大幅に減少 (81.7→79.4%) した。また、ソーキング処理時のアルカリ添加率が増加するに従い不透明度は低下傾向にあった (Fig. 8)。

LBKP のシート比散乱係数は、過酸化水素のみ添加のソーキング処理を行うことで (Table 1 (c)), ソーキング未処理 (Table 1 (b)) と比較して低下 (454→430 cm²/g) した。また、ソーキング処理時のアルカリ添加率が 3 % を超えると大幅に低下した (Fig. 9)。

2) TMP

同一緊度で比較した場合、TMP もソーキング処理工程として過酸化水素のみ添加のソーキング処理を行うことで (Table 2 (c)), ソーキング未処理 (Table 2 (b)) に比べ、不透明度は大幅に減少 (97.2→94.4%) した。また、ソーキング処理時のアルカリ添加により不透明度は大幅に減少していた (Fig. 8)。

TMP のシート比散乱係数は、過酸化水素のみ添加のソ

ーキング処理を行うことで (Table 2 (c)), ソーキング未処理 (Table 2 (b)) と比べて変化 (553→555 cm²/g) は認められなかった。また、TMP はソーキング処理時にアルカリを添加した場合の変化は、バラツキが大きく、一定の傾向は認められなかった (Fig. 9)。

3.1.4 ソーキング処理におけるアルカリ添加率の影響に関する考察

1) LBKP

未乾燥の場合に比べ、抄紙・熱乾燥・再離解することで、フリーネスは増加し、ファイン分が減少した。また、作製したシートは、未乾燥のパルプから作製したシートと比較して緊度が大幅に低下した。また、同一緊度で比較して、比引裂強さや比引張り強さが低下した。これらから、抄紙・熱乾燥・再離解の処理によって、繊維間結合力に寄与していたファイン分、あるいはフィブリルが除去された結果、繊維間結合量が大幅に減少したのではないかと考えられる。しかし、離解後にソーキング処理工程として、過酸化水素のみ添加の温浴処理を行った場合、ソーキング未処理と比較して比散乱係数は低下し、比引裂強さや比引張り強さが向上した。このことから、ソーキング処理によって繊維間結合がある程度復元したのではないかと考えられる (比破裂度、耐折強度も向上)。また、アルカリと過酸化水素を添加してソーキング処理を行った場合には、アルカリの添加率に伴って比引裂強さや比引張り強さが低下する傾向を示したが、フリーネスはほとんど変化せず、比散乱係数は低下傾向を示した。これらのことから、アルカリを添加した場合は繊維間結合が減少したのではなく、パルプ単繊維自体がダメージを受けたものと推測される (比破裂度、耐折強度も低下)。

2) TMP

抄紙・乾燥・熱履歴を経て再離解することでフリーネスは増加し、ファイン分が減少した。しかし LBKP とは異なり、再離解パルプで作製したシートは、未乾燥のそれと比較して緊度が若干増加した。同一緊度で比較して、未乾燥パルプで作製したシートより比引裂強さや比引張り強さが向上したことから、抄紙・熱乾燥・再離解の処理によって繊維間結合に寄与していなかったファイン分 (例えばリグニンリッチなファインなど) が除去されることで、繊維間結合力が増加したのではないかと考えられる。しかし、離解後にソーキング処理工程として、過酸化水素のみ添加の温浴処理を行った場合、ソーキング未処理と比較してフリーネスが大幅に増加し、比引裂強さや比引張り強さが低下したことから、繊維間結合が減少したものと推測される。しかし、比散乱係数には変化が認められないことから、ソーキング処理後の終 pH が 4.9 という条件下でのソーキング処理が単繊維強度低下に影響していることも考えられる。また、アルカリと過酸化水素を添加してソーキング処理を行った場合には、アルカリ添加率が対パルプ 2 % を境として挙動が異なり、2 % 未満ではソーキング未処理よりフリーネスは増加し、比引裂強さも同一緊度で比較してソーキング未処理と同程度まで回復した。しかし、2 % を超えるとソーキング未処理よりフリーネスは減少し、比引

Table 5 Pulp and sheet properties (HBKP)

Effects of alkaline peroxide treatment on the pulp and sheet properties at a different peroxide charge

Alkaline charge (%)	3.6				
Peroxide charge (%)	0	0.45	0.9	1.35	1.8
Fiber length (mm)	0.585	0.585	0.590	0.585	0.600
Fines (%)	0.61	0.61	0.61	0.64	0.63
Cell wall thickness (μm)	4.6	4.5	4.7	4.6	4.7
CSF (ml)	515	510	505	500	470
A fixed pressure (3.5 kg/cm ²)					
Sheet density (g/cm ³)	0.552	0.557	0.559	0.567	0.574
A fixed sheet density (g/cm ³)	0.6				
Tear index (mN·m ² /g)	6.0	6.4	6.8	6.5	6.4
Tensile index (N·m/g)	37	38	38	39	41
Opacity (%)	80.9	79.4	79.0	78.9	78.1
Scattering coefficient (cm ² /g)	443	440	435	430	416
ISO Brightness (%)	84.2	88.8	89.4	89.7	89.9

Table 6 Pulp and sheet properties (TMP)

Effects of alkaline peroxide treatment on the pulp and sheet properties at a different peroxide charge

Alkaline charge (%)	3.6				
Peroxide charge (%)	0	0.45	0.9	1.35	1.8
Fiber length (mm)	1.390	1.400	1.440	1.410	1.410
Fines (%)	1.49	1.44	1.39	1.43	1.45
Cell wall thickness (μm)	8.9	8.8	8.8	8.9	8.6
CSF (ml)	170	160	160	150	145
A fixed pressure (3.5 kg/cm ²)					
Sheet density (g/cm ³)	0.389	0.397	0.397	0.398	0.398
A fixed sheet density (g/cm ³)	0.4				
Tear index (mN·m ² /g)	7.7	8.0	7.8	7.7	7.6
Tensile index (N·m/g)	38	39	39	39	39
Opacity (%)	97.1	95.2	94.1	92.2	91.4
Scattering coefficient (cm ² /g)	528	521	553	550	558
ISO Brightness (%)	45.8	52.2	58.1	63.4	66.9

裂強さも低下傾向を示した。これらのことから、ソーキング中の pH が繊維強度に影響し、高 pH により強度が低下すると推測される。TMP は LBKP と比較した場合、リグニンに保護されているため、ソーキング処理時のアルカリ添加率の影響を受けにくいものの、添加率が高い場合にはパルプの単繊維強度も影響を受けるものと考えられる。ま

た、アルカリ処理で比引張り強さは若干向上する傾向にあるが、比散乱係数はほとんど変化が認められないことから、繊維間結合量の増加とは異なるメカニズムによって繊維間の結合力が増加したと考えられる。ソーキング処理による不透明度の低下は、アルカリ条件下における過酸化水素の活性化によって、白色度が 9 pts. 程度向上したことによる

と考えられる。

3.2 ソーキング処理における過酸化水素添加率の影響

次に、ソーキング処理において、アルカリを一定添加(対パルプ 3.6% as NaOH)で固定し、過酸化水素の添加率を変動させてパルプ物性に与える影響について検討を行った。パルプ物性、シート物性の一覧を Table 5, Table 6 に示す。また、過酸化水素添加なし(アルカリ 3.6% のみ)の結果を、比較のために Table 1 (d), Table 2 (d) に示す。

3.2.1 パルプ物性、シート緊度

1) LBKP

一度、抄紙・乾燥・熱履歴を経た後再離解し、ソーキング処理工程として、アルカリのみ添加の温浴処理(終 pH 12.7)を行ったパルプのパルプ特性、及びそのパルプを用いて作製したシートの緊度を Table 1 (d) に示す。ソーキング未処理のパルプの物性(Table 1 (b))と比較し、フリーネスは増加(470→515 ml)し、また、このパルプで作製したシートは、ソーキング未処理のパルプから作製したシートと比較して、緊度が大幅に低下(0.576→0.552 g/cm³)した。また、ソーキング処理時の過酸化水素添加率が増加(終 pH 12.6~11.8)するに伴い、パルプのフリーネスは低下(Fig. 10)、緊度は増加する傾向を示した(Fig. 11)。

Fig. 10 Effects of alkaline peroxide treatment on the C. S. F. at a different peroxide charge

Fig. 11 Effects of alkaline peroxide treatment on the sheet density at a different peroxide charge

2) TMP

TMP は LBKP とは若干異なる挙動を示した。抄紙・熱乾燥を経て再離解後に、ソーキング工程として、アルカリのみ添加の温浴処理(終 pH 10.8)を行ったパルプのパルプ特性、及びそのパルプで作製したシートの緊度を Table 2 (d) に示す。ソーキング未処理のパルプ(Table 2 (b))と比較し、フリーネスは増加(105→170 ml)し、ファイン分も増加(1.13→1.49%)したが、繊維壁厚は同等(8.9→8.9 μm)であった。このパルプで作製したシートは(Table 2 (d)), ソーキング未処理のパルプを用いて作製したシートと比較し、緊度が低下(0.398→0.389 g/cm³)した。また、ソーキング処理時に過酸化水素を添加した場合、パルプのフリーネスは添加率に応じて減少したが(Fig. 10)、緊度は過酸化水素の有無だけに相関があり、添加率の違いが与える影響は、ほとんど認められなかった(Fig. 11)。

3.2.2 シート特性

1) LBKP

抄紙・熱乾燥を経て再離解後にソーキング処理工程として、アルカリのみ添加のソーキング処理を行った場合(Table 1 (d)), ソーキング未処理(Table 1 (b))と同一緊度で比較して、比引張強さは同等(37→37 N·m/g)であったが、比引裂強さは大幅に低下(7.1→6.0 mN·m²/g)した。そして、ソーキング処理時の過酸化水素添加率が増加するに伴って、比引裂強さは極大値を示した(Fig. 12)

Fig. 12 Effects of alkaline peroxide treatment on the tear index at a different peroxide charge

Fig. 13 Effects of alkaline peroxide treatment on the tear index at a different peroxide charge

が、比引張強さは単調に増加した (Fig. 13)。

2) TMP

抄紙・熱乾燥を経て再離解後にアルカリのみ添加のソーキング処理を行った場合 (Table 2 (d)), ソーキング未処理 (Table 2 (b)) と比較して比引裂強さは若干低下 ($7.9 \rightarrow 7.7 \text{ mN} \cdot \text{m}^2/\text{g}$) し、比引張強さも低下 ($42 \rightarrow 38 \text{ N} \cdot \text{m}/\text{g}$) した。また、ソーキング処理時の過酸化水素添加率増加に伴い、比引裂強さは過酸化水素少量添加で極大値を示し、(Fig. 12), 比引張強さは若干増加傾向にあった (Fig. 13)。

3.2.3 光学特性

1) LBKP

同一緊度で比較した場合、ソーキング未処理 (Table 1 (b)) に対し、ソーキング処理工程としてアルカリのみ添加のソーキング処理を行うことで (Table 1 (d)), シートの不透明度は減少 ($81.7 \rightarrow 80.9\%$) し、比散乱係数も減少 ($454 \rightarrow 443 \text{ cm}^2/\text{g}$) した。また、ソーキング処理時の過酸化水素添加率増加に伴って、比散乱係数は低下し (Fig. 14), 不透明度も大幅に低下した (Fig. 15)。

2) TMP

同一緊度で比較した場合、ソーキング未処理 (Table 2 (b)) に対し、ソーキング処理工程としてアルカリのみ添

加のソーキング処理を行っても不透明度はほぼ同等 ($97.2 \rightarrow 97.1\%$) であった (Table 2 (d))。また、シートの比散乱係数は、ソーキング未処理 (Table 2 (b)) に対し、アルカリのみ添加のソーキング処理を行うことで減少 ($553 \rightarrow 528 \text{ cm}^2/\text{g}$) した (Table 2 (d))。また、ソーキング処理時の過酸化水素添加率増加に伴って、比散乱係数は増加傾向を示し (Fig. 14) 不透明度は大幅に減少した (Fig. 15)。

3.2.4 ソーキング処理における過酸化水素添加率の影響に関する考察

1) LBKP

抄紙・熱乾燥を経て離解後にソーキング処理工程として、アルカリのみ添加の温浴処理を行った場合、ソーキング未処理と比較して比散乱係数は低下し、比引張り強さは同等で、比引裂強さは大幅に低下した。これらのことから、終 pH 12.7 という高 pH 条件下でのソーキング処理によって、パルプ単繊維自体がダメージを受けたと考えられる。しかし、過酸化水素の添加率増加に伴って比引張り強さは増加し、これがフリーネス低下 (Fig. 16) や、比散乱係数低下 (Fig. 17) との相関が非常に高いことから、過酸化水素を含むソーキング (アルカリ過酸化水素漂白) 処理によって、繊維間結合がある程度復元したと考えられる。ただ

Fig. 14 Effects of alkaline peroxide treatment on the scattering coefficient at a different peroxide charge

Fig. 16 Correlation between C.S.F. and tensile index

Fig. 15 Effects of alkaline peroxide treatment on the opacity at a different peroxide charge

Fig. 17 Correlation between scattering coefficient and tensile index

Fig. 18 Correlation between opacity and scattering coefficient

し、繊維間結合量が増加し、比散乱係数は低下したため、不透明度が大幅に低下したと考えられる (Fig. 18)。

2) TMP

抄紙・熱乾燥を経て離解後にソーキング処理工程として、アルカリのみ添加の温浴処理を行うことでフリーネスが大幅に増加し、比引裂強さや比引張り強さが低下したことから、繊維間結合が減少したと考えられる。また、過酸化水素添加率増加に伴って比引張り強さは増加傾向を示したが、このことはフリーネス低下 (Fig. 16) との相関があるものの、比散乱係数とは相関が低い (Fig. 17) ことから、繊維間結合量の増加とは異なるメカニズムによって繊維間の結合力が増加したと考えられる。TMP は LBKP と比較した場合、リグニンに保護されているため、ソーキング処理時の過酸化水素添加の影響を受けにくいものの、比引裂強さが若干減少傾向であることから、パルプ単繊維の強度は低下すると考えられる。また、不透明度の低下に伴い、比散乱係数が増加することから、TMP の不透明度低下は繊維間結合量の増加ではなく、ソーキング処理における白色度向上 (11 pts. 程度, Fig. 19) が大きく影響していると考えられる (Fig. 20)。

Fig. 19 Effects of alkaline peroxide treatment on the brightness at a different peroxide charge

Fig. 20 Correlation between opacity and brightness

4. 結 論

従来、古紙のリサイクルテストにおいて、抄紙、乾燥、再離解を繰り返すことで、パルプは単純に劣化していくと考えられていた。本報では、実際の古紙処理で行われる脱インキ工程に則したアルカリ性薬品による脱インキ処理を考慮した場合、単に湿潤・乾燥を繰り返したりサイクルテストとは異なり、パルプの違いによる劣化の程度、ソーキング処理の有無による紙力への影響、ソーキング処理時のアルカリ添加率、過酸化水素添加率による紙力への影響など、古紙の種類や処理工程によって、処理後のパルプ物性が大きく異なることを示した。

LBKP は、抄紙・乾燥・熱履歴を経て、再離解後にソーキング処理工程を行った場合、

- ① ソーキング未処理のパルプと比較して比引裂強さは低下したが、比散乱係数が低下するとともに比引張り強さが向上した。
- ② 過酸化水素添加率 1.8% 一定でアルカリ添加率を増加させることで、比引裂強さが顕著に低下したが、比散乱係数は低下傾向であった。
- ③ アルカリ添加率 3.6% 一定で過酸化水素の添加率を増加させることで、比散乱係数が低下するとともに比引張り強さが向上した。

以上より、ソーキング処理におけるアルカリの作用により、単繊維自体はダメージを受け、過酸化水素の作用により繊維間結合量は増加すると考えられる。

これに対し、TMP は、抄紙・乾燥・熱履歴を経て再離解後にソーキング処理工程を行った場合、

- ① ソーキング未処理のパルプと比較して、若干比引裂強さや比引張り強さが低下したが、LBKP より低下幅は小さかった。
- ② 過酸化水素添加率 1.8% 一定でアルカリ添加率を増加させることで、低下幅は小さいが、比引裂強さは若干低下傾向を示した。比引張り強さはソーキング処理で若干向上する傾向にあるが、比散乱係数はほとんど変化が認められなかった。

- ③ アルカリ添加率 3.6% 一定で過酸化水素の添加率を増加させることで、比引裂強さは若干減少傾向であり、比散乱係数と比引張り強さは増加傾向を示した。

以上より、ソーキング処理におけるアルカリの作用による単繊維自体のダメージは少なく、過酸化水素の作用により繊維間結合量が若干増加すると考えられる。

5. おわりに

以上、本報では LBKP, TMP それぞれの単独パルプによるリサイクルデータのみを記載したが、LBKP と TMP を混合してリサイクルテストを行った場合、単純な加重平均にならない物性が出てくることを既にラボテストで確認しており、今後更に研究を進めていく必要があると考えている。更に、今回はリサイクルテストにソーキング（アルカリ過酸化水素漂白）処理を加えて考察したが、リサイクル回数を増加していった場合の挙動についても、パルプ物性だけでなく、印刷適性などの影響も考慮して今後検討していく必要がある。

これらの結果は、目的の製品品質に応じて、古紙原料、および脱インキ処理工程の選択を行うことで、パルプ物性の調整を行える可能性を示唆している。特に、リサイクルによる著しい物性低下の抑制を検討する上で、これらの知見を生かすことが重要であると考えている。

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(受理：'07.8.23)

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1. Introduction

Recently, concern for environment preservation is in a high tide, and products friendly to recycling are in demand. It is requested to develop new paper products which use recycled pulp. Increasing recycled pulp ratios in current products is also wanted, and we have to promote paper recycling ever more. On the other hand, high quality product demands recycled pulp of high quality that is as good

as fresh pulp. So, we need to know how recycling affects pulp quality.

There have been many studies on recycling of waste paper, like selecting wood species suitable for recycling and quality change of pulp by recycling. The method for testing recycling was to prepare wet hand sheets from repulped waste paper, to dry them, and then to repulp them to prepare hand sheets once again. Most of studies did not use chemicals in their recycling tests, and most of their

evaluations of pulp strength were not based on the same sheet density value¹⁻⁷⁾.

Commercial recycling processes for waste paper are requested to produce recycled pulp whose quality is as good as or better than that of its original waste paper. They have deinking processes in their lines which use alkaline chemicals like sodium hydroxide. When brightness higher than that of original waste paper is wanted, recycled pulp is bleached with hydrogen peroxide under an alkaline condition.

The effect of alkaline chemicals and hydrogen peroxide on pulp quality has been discussed from the stand point of pulp swelling and bonded area increase. Most of papers were studies on them when TMP and CTMP were produced⁸⁻¹⁵⁾. Some papers investigated on the evaluation of recycling. But, they were either studies with adding each chemical at the same amount¹⁶⁾¹⁷⁾ or one just with disintegration and without soaking (alkaline hydrogen peroxide treatment)¹⁸⁾. There has been no paper studying the effect on pulp quality by soaking at different chemical addition levels with pulp, LBKP or TMP, which had been formed to sheet, dried by heat and then repulped beforehand. In order to simulate deinking processes in mills, our recycling test was done with chemical addition similar to those in commercial deinking processes, different from the experiment of simple wet and dry cycle. Moreover, the pulp quality change was evaluated at the same sheet density level

2. Experiment

Once pulp is formed in sheet and is dried (thermal treatment), it is generally believed that pulp gets solidified and its ability for bonding decreases. Deinking processes for paper recycling usually have soaking (alkaline hydrogen peroxide bleaching) as one of treatments. Amounts of chemicals used at the soaking depend on quality of waste paper and quality of recycled pulp desired. In general, their addition rates, percent on pulp, are as follows. Sodium hydroxide : 0.5–3.0% Sodium silicate : 1.0–5.0% Deinking chemical : 0.01–0.5% Hydrogen peroxide : 0.2–3.0% Whether soaking is present in the process or not will affect recycled pulp quality very much. So, the effects of chemicals like sodium hydroxide, the inhibitor of discoloration caused by sodium hydroxide and hydrogen peroxide on pulp quality were studied by changing their addition rates.

2.1 Experimental scheme

1) At first, a pulp sample was selected as starting pulp. It was formed to hand sheets. The quality of the pulp and the hand sheets was studied as in Fig.1 and Fig.2. Their qualities are in Table 1 (a) and Table 2 (a). Then, the hand sheets, after dried by heat, were repulped, and

formed to hand sheets again. The quality of the repulped pulp and its hand sheets were investigated. They were summarized in Table 1 (b) and Table 2 (b).

2) The repulped pulp was used as a starting sample for studying the effect of alkaline in alkaline soaking, keeping hydrogen peroxide addition at a fixed rate.

3) Using the same repulped pulp, the effect of hydrogen peroxide was studied, keeping the rate of alkaline addition at a fixed value.

The scheme of the experiment is summarized in Fig. 3.

2.2 Soaking treatment with various levels of alkaline addition

Sample pulps were LBKP (*Eucalyptus globules*/*Acacia auriculiformis*, 450 ml CSF, 82.5% ISO) and TMP (*Picea jezoensis*/*Abies sachalinensis*/*Picea glauca*, 90 ml CSF, 52.9% ISO). They were produced at a mill and were delivered to us as wet pulp. They were formed to hand sheets, dried by heat respectively as shown in Fig.1 and Fig.2. These dried hand sheets were the starting samples for soaking treatment.

Using these starting pulps, soaking was done following a procedure in Fig. 3. The starting pulp, to which sodium hydroxide was added at 0.4% based on pulp, was repulped in a test pulper at the consistency of 2 percent for 20 minutes. Please note that all addition rates of chemicals were expressed as pure chemical basis in this paper.

Then, the pulp was dewatered to the consistency of 35%, to which sodium hydroxide and sodium silicate were added. Then, hydrogen peroxide was added and the pulp consistency was adjusted to 25%. The pulp was kept for 2.5 hours at 60°C in a constant temperature water bath for soaking treatment (alkaline hydrogen peroxide bleaching). A ratio of hydrogen peroxide to the pulp was fixed to 1.8%. As for sodium hydroxide and sodium silicate, their total alkaline addition was varied from 0% to 3.6% based on pulp. The total alkaline was defined as sodium hydroxide, and that of sodium silicate was obtained by multiplying 0.311 to its weight. The ratio of sodium hydroxide to sodium silicate was 70/30 as NaOH. After the soaking, the pulp was diluted to 1.5%, and was disintegrated by a test pulper for 2 minutes. Then, it was neutralized in pH by adding sulfuric acid while it was being disintegrated for 1 minute. Its pulp quality was measured. The pulp was also formed to hand sheets at the fixed basis weight, was pressed at the standard pressure (3.5 kg/cm²), and was air dried as in JIS P 8222. Due to different soaking conditions, their hand sheets were not the same in the sheet density. To get physical properties at the same sheet density, we took a following procedure. Hand sheets were grouped to several groups. Every group was pressed at a different pressure to get hand sheets of a different sheet density. Each physical property measured was plotted

against those sheet densities to interpolate the value at a certain fixed sheet density.

Physical properties measured with hand sheets were tear index (JIS P 8116), burst factor (JIS P 8113) and folding endurance (JIS P 8112). Optical properties measured were brightness (JIS P 8226) and opacity and scattering coefficient (JIS P 8149). Fiber length, fine fraction ratio and fiber wall thickness were measured by KAJAANI Fiber Lab (JIS P 8226).

2.3 Soaking treatment with various levels of hydrogen peroxide addition

The hand sheets of the starting pulp described in Fig. 1 and Fig. 2 was repulped, dewatered and treated by soaking by the procedure in Fig. 3. The total alkaline was fixed at 3.6% as NaOH based on pulp. The ratio of sodium hydroxide to sodium silicate was 70/30. It was equivalent to the composition in which sodium hydroxide was 2.5% and sodium silicate was 3.3% (1.1% as NaOH).

After disintegration, hydrogen peroxide was added to the pulp at different addition rates ranging from 0 to 1.8%. The other procedure was the same as in 2.2. The quality of the pulp and its hand sheets were evaluated

3. Result and discussion

3.1 Effect of alkaline addition in soaking

Hydrogen peroxide was fixed at 1.8% on pulp, and the effect of alkaline addition was studied by changing its addition rate. The physical properties of pulps and their hand sheets are summarized in Table 3 and Table 4. As reference, those of the soaking in which only hydrogen peroxide was added at the rate of 1.8% without alkaline are in Table 1 (c) and Table 2 (c).

3.1.1 Physical properties of pulp and sheet density

1) LBKP

LBKP was commercially produced at a mill, was delivered to us as wet pulp (not dried) and was refined to freeness of 450 ml. It was formed to hand sheets, dried by heat and repulped. Then, the repulped pulp was treated with soaking, in which only hydrogen peroxide was added (1.8% based on pulp), in a warm bath. The final pH was 5.1. The fiber properties of these three pulps, original LBKP, repulped one and one after the soaking, and the physical properties of their hand sheets were measured, and were summarized in Table 1, along with their sheet densities.

Compared with the starting pulp (original LBKP), the pulp which had been formed to sheets, dried by heat and then repulped showed higher freeness (470 ml from 450 ml), less fine fraction ratio (0.57% from 0.68%) and less fiber wall thickness ($4.7 \mu\text{m}$ from $5.3 \mu\text{m}$). Its hand sheet density was greatly reduced to 0.576 g/cm^3 from 0.671 g/cm^3 .

When the dried and repulped pulp was treated by soaking with only hydrogen peroxide, the treatment increased the freeness to 480 ml from 470 ml and the sheet density to 0.584 g/cm^3 from 0.576 g/cm^3 as in Table 1 (c). Adding more alkaline in the soaking, whose final pH was 11.1–11.7, did not cause noticeable change in freeness (Fig. 4) and sheet density (Fig. 5).

2) TMP

TMP behaved differently from LBKP. TMP, which was commercially produced in a mill, and whose retency was removed, was the starting pulp. It was formed to sheets, was dried by heat, and was repulped. Then, the resulting pulp was treated with soaking, in which only hydrogen peroxide was added, in a warm bath. The final pH was 4.9.

The fiber properties of these three pulps and the physical properties of their hand sheets were measured, and were summarized in Table 2, along with their sheet densities.

Compared with the starting pulp (not dried) (Table 2 (a)), the dried and repulped pulp (Table 2 (b)) showed higher freeness (105 ml from 90 ml), and less fine fraction (1.13% from 1.26%). The fiber wall thickness was almost at the same value ($8.9 \mu\text{m}$ from $8.6 \mu\text{m}$). The sheet density of this pulp slightly increased to 0.398 g/cm^3 from 0.386 g/cm^3 (Table 2 (b)).

When the dried and repulped pulp was treated by soaking with hydrogen peroxide only, the treatment increased the freeness to 145 ml from 105 ml. In spite of the higher freeness, the fine fraction increased to 1.26% from 1.13% and the fiber wall thickness was almost at the same value ($8.6 \mu\text{m}$ from $8.9 \mu\text{m}$). The sheet density was greatly reduced to 0.584 g/cm^3 from 0.576 g/cm^3 as in Table 1 (c).

Adding alkaline in the soaking, whose rate was less than 2% on pulp and whose final pH was less than 8, increased the freeness as in Fig. 5 and also slightly increased the sheet density as in Fig. 4. When the alkaline charge was over 2% and final pH was more than 8, the freeness tended to decrease as in Fig. 5 and the sheet density greatly increased as in Fig. 4 with increasing alkaline charge.

3.1.2 Physical properties of hand sheet

1) LBKP

Hand sheets prepared were evaluated at the same sheet density as described in 2.2. Hand sheets of LBKP, which had been formed to sheets, dried by heat and then repulped, (Table 1 (b)) were compared with those of not dried LBKP (Table 1 (a)). Its tear index was down from $8.5 \text{ mN}\cdot\text{m}^2/\text{g}$ to $7.1 \text{ mN}\cdot\text{m}^2/\text{g}$, and its tensile index was also down from $58 \text{ N}\cdot\text{m}/\text{g}$ to $37 \text{ N}\cdot\text{m}/\text{g}$.

When it was treated by soaking with only hydrogen peroxide (Table 1 (c)), the tear index was improved from $7.1 \text{ mN}\cdot\text{m}^2/\text{g}$ to $7.8 \text{ mN}\cdot\text{m}^2/\text{g}$, and the tensile index was

also improved from $37 \text{ N} \cdot \text{m/g}$ to $43 \text{ N} \cdot \text{m/g}$.

But, adding alkaline at the soaking greatly decreased the tear index (Fig. 6) and the more alkaline enhanced the effect. The tensile index also showed the same downward trend (Fig. 7).

2) TMP

Hand sheets of TMP, which had been formed to sheets, dried by heat and then repulped, were compared with those of not dried TMP. Different from LBKP, its tear index improved from $7.3 \text{ mN} \cdot \text{m}^2/\text{g}$ to $7.9 \text{ mN} \cdot \text{m}^2/\text{g}$, and its tensile index also improved from $38 \text{ N} \cdot \text{m/g}$ to $42 \text{ N} \cdot \text{m/g}$.

When it was treated by soaking with only hydrogen peroxide (Table 2 (c)), the tear index decreased from $7.9 \text{ mN} \cdot \text{m}^2/\text{g}$ to $7.2 \text{ mN} \cdot \text{m}^2/\text{g}$, and its tensile index also decreased from $42 \text{ N} \cdot \text{m/g}$ to $38 \text{ N} \cdot \text{m/g}$.

When alkaline was added whose rate was less than 2% per pulp, the tear index increased as in Fig. 6. When the rate was increased over 2%, the tear index tended to decrease. As for the tensile index, alkaline addition of less than 2% did not cause any effect. When it was over 2%, the tensile index slightly improved (Fig. 7).

3.1.3 Optical properties

1) LBKP

Optical properties were compared at the same sheet density. LBKP was treated by soaking only with hydrogen peroxide. The soaking reduced opacity to 79.4% from 81.7% which was the value before the soaking. (Table 1 (b) and Table 1 (c)) When alkaline was added in the soaking, the opacity tended to decrease with increasing alkaline addition (Fig. 8).

The sheet scattering coefficient was reduced from $454 \text{ cm}^2/\text{g}$ to $430 \text{ cm}^2/\text{g}$ by the soaking with hydrogen peroxide alone. (Table 1 (c) and Table 1 (b)) When the alkaline addition became more than 3%, the decrease was greatly enhanced (Fig. 9).

2) TMP

Every comparison was made at the same sheet density. When TMP was treated by soaking with only hydrogen peroxide, its opacity decreased very much from 97.2% to 94.4%. (Table 2 (c) and Table 2 (b)) When alkaline was added at the soaking, its opacity greatly reduced (Fig. 8).

The sheet scattering coefficient did not change so much by the soaking with hydrogen peroxide only, which was from $553 \text{ cm}^2/\text{g}$ to $555 \text{ cm}^2/\text{g}$. When alkaline was added at the soaking, no definite trend was observed (Fig. 9).

3.1.4 Discussion on effect of alkaline addition at soaking.

1) LBKP

LBKP which had been formed to sheets, dried by heat and repulped beforehand was compared with original not dried one. Its freeness increased and its fine fraction ratio

decreased. The sheets formed from it had much lower sheet density than those of not dried pulp. When they were compared with each other at the same sheet density, the former gave less tear index and less tensile index. We assume that the loss of strength was due to less inter-fiber bonding volume, which was caused by losing fine fraction and/or fibrils, main contributors to fiber bonding, by successive sheet forming, drying and repulping.

When the repulped pulp was treated by soaking with only hydrogen peroxide at a warm temperature, its scattering coefficient decreased. On the other hands, its tensile index and tear index increased. The fact suggested that the soaking might recover some inter-fiber bonding.

When alkaline was added along with hydrogen peroxide in the soaking, its tear index and tensile index tended to decrease with increasing alkaline amount. On the other hands, its freeness did not change and its scattering coefficient decreased. It seemed that the loss of strength of this case was due to damage on fiber itself caused by alkaline, not by losing inter-fiber bonded area. We observed that burst factor and folding endurance also decreased.

2) TMP

TMP which had been formed to sheets, dried by heat and repulped was compared with original not dried one. Its freeness increased and its fine fraction ratio decreased. Different from LBKP, the sheets formed from it had slightly larger sheet density than those of not dried pulp. When they were compared with each other at the same sheet density, the former had higher tear index and tensile index. It may suggest that the treatment of sheet forming, drying and repulping in series might get rid of some unwanted fine to fiber bonding like that of high lignin content and therefore improved fiber bonding.

When the repulped pulp was treated by soaking with hydrogen peroxide alone in a warm temperature, its freeness greatly increased and its strength like tear index and tensile index decreased. It may suggest that the inter-fiber bonded area decreased. But, there was no change observed in scattering coefficient. So, it may be more reasonable to think that the soaking which ended at pH 4.9 might damage intrinsic fiber strength itself.

When alkaline was added at the soaking along with hydrogen peroxide, the addition rate of 2% separated the behavior of the pulp. In a zone where the addition rate was less than 2%, its freeness increased and its tear index recovered to the level before the soaking, when compared at the same sheet density. In a zone over 2%, its freeness was less than that before the soaking and its tear index started to decline. It suggests that the pH at the soaking affected intrinsic fiber strength and the higher pH might deteriorate it. As TMP was protected by lignin more than LBKP, it was less affected by alkaline at the soaking. How-

ever, when alkaline addition was high enough, its intrinsic fiber strength was also damaged.

As the alkaline addition slightly improved tensile index, and did not cause any observable change in scattering coefficient, the inter-fiber bonding force might increased by a mechanism other than the increase of fiber bonded area. The loss of opacity by the soaking was due to the brightness increase which was 9 points by hydrogen peroxide activity

3.2 Effect of hydrogen peroxide addition at soaking

As a next series of experiment, alkaline was fixed at 3.6% as NaOH per pulp in the soaking, and the effect of hydrogen peroxide addition on pulp qualities was studied. The pulp qualities and sheet qualities are in Table 5 and Table 6. As reference, those of a trial in which only alkaline (3.6%) was added without hydrogen peroxide are in Table 1 (d) and Table 2 (d).

3.2.1 Pulp qualities and sheet density

1) LBKP

LBKP which had been formed to sheet, dried by heat and then repulped was treated by soaking only with alkaline in a warm water bath. The final pH was 12.7. Its qualities and sheet density are in Table 1 (d). Comparing them with those before the soaking (Table 1 (b)), the soaking increased freeness from 470 ml to 515 ml, and decreased sheet density from 0.576 g/cm³ to 0.522 g/cm³. When hydrogen peroxide was added in the soaking, the freeness tended to decreased with increasing hydrogen peroxide amount whose final pH was between 12.6 and 11.8 (Fig. 10). The sheet density tended to increase (Fig. 11).

2) TMP

TMP behaved in a somewhat different way. TMP which had been formed to sheet, dried by heat and then repulped was treated by soaking only with alkaline in a warm water bath. Its final pH was 10.8. Its qualities and sheet density are in Table 2 (d). Compared with those before the soaking (Table 2 (b)), its freeness increased from 105 ml to 170 ml and its fine fraction ratio also increased from 1.13% to 1.49%. However, its fiber wall thickness was almost the same from 8.9 μm to 8.9 μm. The sheet density of this pulp was down to 0.389 g/cm³ from 0.398 g/cm³ by the soaking.

When hydrogen peroxide was added in the soaking, the freeness tended to decreased with increasing hydrogen peroxide amount (Fig. 10). Regarding the sheet density, whether hydrogen peroxide was present or not was an affecting factor, and the addition rate did not make any difference (Fig. 11).

3.2.2 Physical properties of sheet

1) LBKP

LBKP which had been formed to sheet, dried by heat

and then repulped was treated by soaking only with alkaline. Its sheet properties (Table 1 (d)) were compared with those of pulp before the soaking (Table 1 (b)) at the same sheet density. Its tear index was almost the same to that before the soaking from 37 N·m/g to 37 N·m/g. Its tensile index was much down from 7.1 mNm²/g to 6.0 mNm²/g.

Then, hydrogen peroxide was added to the soaking. By increasing its addition rate, the tear index gave the maximum (Fig. 12), and the tensile index simply increased (Fig. 13).

2) TMP

TMP which had been formed to sheet, dried by heat and then repulped was treated by soaking only with alkaline. Compared with those of TMP before the soaking, its tear index slightly decreased from 7.9 mNm²/g to 7.7 mNm²/g, and its tensile index also decreased from 42 N·m/g to 38 N·m/g Please see Table 2 (d) and Table 2 (b).

By increasing the addition rate of hydrogen peroxide at the soaking, the tear index gave the maximum in a zone of low addition rate (Fig. 12), and the tensile index gradually increased (Fig. 13).

3.2.3 Optical properties

1) LBKP

When compared at the same sheet density, the soaking treatment with only hydrogen peroxide (Table 1 (c)) reduced opacity to 76.4% from 81.7%, which was the value before the soaking (Table 1 (b)). The same effect was observed on scattering coefficient from 454 cm²/g to 443 cm²/g. Increasing hydrogen peroxide addition at the soaking enhanced the effect (Fig. 14 and Fig. 15)

2) TMP

Optical properties were compared at the same sheet density. The soaking with only alkaline did not change opacity, which was from 97.2% to 97.1% (Table 2 (d)). The treatment reduced sheet scattering coefficient from 553 cm²/g to 528 cm²/g (Table 2 (d)). Increasing hydrogen peroxide addition at the soaking tended to increase the scattering coefficient (Fig. 14), and greatly decreased the opacity (Fig. 15).

3.2.4 Discussion on effect of hydrogen peroxide addition in soaking

1) LBKP

LBKP, which had been formed to sheets, dried by heat and then repulped, was treated with soaking only with alkaline at a warm temperature. It was compared with one before the soaking. The soaking reduced scattering coefficient, did not change tensile index, and reduced tear index. The fact suggests that the soaking, whose final pH was 12.7 and was significantly high, damaged unit fiber itself. When hydrogen peroxide was added at the soaking, the tensile index increased. This increase had a good correlation with the decreases of freeness and scattering coefficient.

cient (Fig. 16 and Fig. 17). It is suggested that the soaking with hydrogen peroxide and alkaline (alkaline hydrogen peroxide bleaching) recovered inter-fiber bonding to some extent. But, the opacity understandably decreased very much, as the inter-fiber bonding increased and the scattering coefficient decreased (Fig. 18).

2) TMP

TMP, which had been formed to sheets, dried by heat and then repulped, was treated by soaking only with alkaline at a warm temperature. It was compared with one before the soaking. The soaking greatly increased freeness, and reduced tear index and tensile index. The fact suggests that inter-fiber bonding decreased. When hydrogen peroxide was added at the soaking, the tensile index increased with increasing amount of hydrogen peroxide. The trend had some correlation with freeness (Fig. 16), and had little correlation with scattering coefficient (Fig. 17). The fact suggests that the inter-fiber bonding increased with a mechanism other than the increase of inter-fiber bonded area. Though TMP, compared with LBKP, is covered with lignin, and will be less affected with hydrogen peroxide in the soaking, its intrinsic fiber strength, nevertheless, is supposed to deteriorated, judging from the fact that its tear index was reduced. Its opacity decreased, though its scattering coefficient increased. It suggests that the opacity loss was by brightness gain by the soaking, which was about 11 points (Fig. 19), not indicating more inter-fiber bonding (Fig. 20).

4. Conclusion

It has been believed that pulp is simply deteriorated by repeating sheet forming, drying and repulping in a series in a recycle test of waste paper. We demonstrated that the deterioration in commercial deinking processes was not so simple as that happens in a simple recycle test of wetting and drying, and conditions in deinking processes greatly affected pulp quality. The factors that mattered were a type of pulp, with or without soaking, conditions of soaking such as addition rate of alkaline and also that of hydrogen peroxide.

When LBKP was treated by soaking after it had been formed to sheet, dried by heat and then repulped in a series, followings were observed.

- ① Compared with LBKP before soaking, its tear index and scattering coefficient decreased. Its tensile index increased.
- ② When hydrogen peroxide was added at a fix rate of 1.8%, and alkaline addition was increased at the soaking, the tear index significantly decreased and the scattering coefficient also tended to decrease.
- ③ When alkaline was added at a fix rate of 3.6%, and hydrogen peroxide addition was increased in the

soaking, the scattering coefficient decreased and the tensile index increased.

These facts suggest that alkaline in the soaking damaged fiber itself and hydrogen peroxide increased inter-fiber bonded area.

When TMP was treated by soaking after it had been formed to sheet, dried by heat and then repulped in a series just like LBKP, followings were observed.

- ① Its tear index and tensile index were slightly down by the soaking. The effects, however, were less than those of LBKP.
- ② When hydrogen peroxide was added at a fixed rate of 1.8%, and alkaline addition was increased at the soaking, the tear index tended to decreased to a small extent and the tensile index tended to increase. The scattering coefficient did not change.
- ③ When alkaline was added at a fixed rate of 3.6%, and hydrogen peroxide addition was increased in the soaking, the tear index tended to decrease slightly. The scattering coefficient and the tensile index increased to some extent.

These facts suggest that damage on TMP fiber itself by alkaline in the soaking was not so significant, and hydrogen peroxide increased inter-fiber bonded area to some extent.

5. Remark

We reported on the recycling of LBKP and that of TMP respectively in this paper. Our follow-up study on mixtures of LBKP and TMP in a lab suggested that their physical properties were not always the same to those of theoretical weighted average, and further study is surely needed. We took into our recycling procedure soaking treatment (alkaline hydrogen peroxide bleaching). It is necessary to study how repeating this procedure will affect not only physical properties but also printability of recycled pulp.

The study of this kind will make it possible to get recycled pulp of desired property by selecting a proper type of waste paper and a suitable condition of deinking. It will also help to suppress deterioration of pulp in recycling.

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