広葉樹 ECF 漂白パルプのヘキセンウロン酸と褪色との関係 (第2報) —ヘキセンウロン酸の褪色機構とサイズプレス処理による褪色抑制—

王子製紙株式会社 基盤技術研究所 第一研究部^{*1} 河江 綾乃, 内田 洋介^{*2}

Relationship between Hexenuronic Acid and Brightness Reversion of ECF-bleached Hardwood Kraft Pulp Part (Part II) —Mechanism of Brightness Reversion and Depressing of the Yellowing by Size-pressed Treatment—

Ayano Kawae and Yosuke Uchida^{*2}

Advanced Technology Laboratory, Oji Paper Co., Ltd.^{*1}

河江綾乃

内田洋介

Abstract

Yellowing of ECF (Elementally Chlorine Free) or TCF (Totally Chlorine Free) bleached pulp has become a significant problem since 1990 s. It has been shown that hexenuronic acid (HexA) is a main cause, but the mechanism of the yellowing is not clear. In order to suppress the yellowing, the removal of HexA from pulp has been conducted by acid treatment, hot chlorine dioxide bleaching, ozone bleaching and others. However, they need a large amount of energy, and decrease pulp yield and strength.

In this report, mechanism of the yellowing was investigated. The results suggest that the yellowing consists of two-stage reactions. The first reaction is the hydrolysis of HexA, and the second one is the reaction of 5-formyl-2-furancarboxylic acid (FFA), which is one of hydrolytic products of HexA. Therefore, it is suggested that the yellowing can be depressed by inhibition of the reaction of FFA.

We found that low molecular weight carboxylic acids (for example, citric acid, tartaric acid and others) and polycarboxylic acid (for example, polyacrylic acid) are useful as a yellowing inhibitor. Size press coating test was carried out as one of the practical ways of adding the inhibitor to the paper. This method was effective to depress the yellowing, while maintaining physical paper properties.

Keywords : Hexenuronic acid, Brightness reversion, Yellowing, Kraft pulp, Hardwood, ECF bleaching, 5-formyl-2-furancarboxylic acid, Polycarboxylic acid, Inhibitor

分類 : K₁ パルプの漂白一般, K₁₂ 無塩素漂白, K₄ クラフトパルプ

1. 緒 言

1990 年代以降, 晒クラフトパルプの漂白方法が従来の塩素漂白法から無塩素漂白法 (ECF 漂白法, TCF 漂白法) に転換されると, 無塩素漂白パルプや無塩素漂白パルプを

^{*1}〒135-8558 東京都江東区東雲 1-10-6/1-10-6
Shinonome, Koto-ku, Tokyo 135-8558, Japan

^{*2}E-mail : yosuke-uchida@ojipaper.co.jp

用いた紙が褪色する問題が散発するようになり、特に酸性紙での褪色が問題となった。褪色の原因については、北欧を中心に白色度が ISO 90% 程度の針葉樹晒クラフトパルプ (NBKP) を主な対象にして研究され、ヘキセンウロン酸 (HexA) の影響が強いことが共通の認識となっている。これに対し、著者らは我が国で標準的なパルプである、白色度が ISO 86% 前後の広葉樹晒クラフトパルプ (LBKP) の褪色原因について調査し、高温高湿下での褪色はやはり HexA の影響が強いことを確認し、第一報にて報告した。また、第一報では LBKP の褪色性に与える漂白シーケンスの影響についても調査し、二酸化塩素主体の ECF 漂白シーケンスで製造した LBKP は HexA が残留しやすく白色度安定性が悪いこと、その原因としては、二酸化塩素による HexA 分解の反応性はリグニン分解のそれより低く LBKP 製造過程で HexA を分解しきれない傾向にあることを挙げ、対策としては未晒クラフトパルプのカッパー価を最適化して、予め漂白パルプ中の HexA/リグニン比を小さくしておくことが有効であることを報告した¹⁾。

従来、HexA に起因する褪色を防止する方法としては、酸処理、高温二酸化塩素処理、オゾン高添加処理等により HexA を除去する方法が知られている²⁻⁷⁾が、これらの処理では副作用として、パルプ収率の低下、パルプ強度の低下、さらには叩解性の低下等がある⁸⁻¹⁰⁾ため、HexA を除去することなく、褪色性を改善する方法の開発が望まれる。

本報告では、HexA に起因する褪色機構を調査し、その結果を基にパルプ中の HexA を除去することなく褪色抑制する方法を見出したので報告する。

2. 実 験

2.1 高 HexA 含有 LBKP の調製と褪色試験

工場製の広葉樹酸素脱リグニンクラフトパルプ (白色度 ISO 55.0%, カッパー価 9.3) を漂白シーケンス D 0-E -P-D 1 で漂白して高 HexA 含有 LBKP (白色度 ISO 83.5%, HexA 含有量 17.6 mmol/kg) を調製した。この高 HexA 含有 LBKP を酸性下 (pH 4.5) で手抄きし、褪色試験用シートとした。褪色試験は、①80℃, 湿度調節なし、②105℃, 湿度調節なし、③80℃, 相対湿度 65% にて行い、3 h, 10 h, 24 h, 48 h 毎に恒温恒湿槽から試験用シートを取り出し、色度 b^* (ISO 5631:2000) を測定した。褪色前後の b^* の差を Δb^* 値とし、褪色度の指標とした。

2.2 モデル化合物による褪色試験 (その 1)

市販濾紙 (アドバンテック No.2) を 0.1 mmol/L 硫酸水に浸し、風乾して酸性濾紙 (紙面 pH 4.5, BD 1 g) を調製した。この酸性濾紙に以下の化合物を単独あるいは組み合わせで添加し、加湿加熱処理 (JIS P 8154-3:2008, 24 h) 前後の b^* を測定し、その差 Δb^* 値から褪色度を評価した。

(試験 1)

- ・2-furancarboxylic acid (FA): 45.5 μ mol
- ・5-formyl-2-furancarboxylic acid (FFA): 4.5 μ mol
- ・塩化鉄 (II), 硫化鉄 (III): 15 μ g
- ・燐酸マンガ (II), 酢酸マンガ (III): 35 μ g

(試験 2)

- ・5-formyl-2-furancarboxylic acid (FFA): 10 μ mol
- ・グルコース, キシロース, マンノース: それぞれ 10 μ mol

(試験 3)

- ・5-formyl-2-furancarboxylic acid (FFA): 10 μ mol
 - ・グルクロン酸, ガラクツロン酸: それぞれ 10 μ mol
- (以上, 和光純薬工業(株)製)

2.3 モデル化合物による褪色試験 (その 2)

工場製の針葉樹晒クラフトパルプ (NBKP) 絶乾 1 g を用い、酸性手抄きシートを調製した (紙面 pH 4.5)。この手抄シートに 10 μ mol の FFA を添加した後、加湿加熱処理 (JIS P 8154-3:2008, 24 h) し、前後の b^* から Δb^* 値を算出し、褪色度を評価した。

2.4 褪色抑制剤の探索実験

2.4.1 低分子カルボン酸の検討

工場製の広葉樹酸素脱リグニンクラフトパルプ (LOKP) をラボで漂白 (D 0-P-D 1 シーケンス) し、高 HexA 含有 LBKP (白色度 ISO 85.3%, HexA 含有量 26.9 mmol/kg) を調製した。これを酸性条件下で手抄きシートを作成し (JIS P 8222:1998), これに低分子カルボン酸 10 種 (クエン酸, 酒石酸, リンゴ酸, 琥珀酸, グリコール酸, 乳酸, グルコン酸, マロン酸, イタコン酸, クエン酸ナトリウム, 全て和光純薬工業(株)製) をそれぞれ対パルプ 5% 含浸させ、風乾した。これらの手抄きシートを、恒温恒湿槽にて加湿加熱処理 (JIS P 8154-3:2008, 24 h 処理) し、処理後の Δb^* からパルプの褪色抑制効果を評価した。また、クエン酸と酒石酸については、薬品添加率を 0.1%, 0.5%, 1% に変更し、同様の実験を行った。

2.4.2 高分子ポリカルボン酸の検討

前記低分子カルボン酸 10 種の代わりに、分子量が異なる 3 種のポリアクリル酸 (PAA, 和光純薬工業(株)製, 平均分子量, 5,000, 25,000, 250,000) を 0.5% 添加し、2.4.1 と同様に褪色抑制効果を調べた。

2.5 クエン酸ナトリウムの外添

2.5.1 クエン酸ナトリウムの添加率の影響

前記高 HexA 含有 LBKP をナイアガラビーターで叩解し、ロジンサイズ剤 (SPYA 50, 荒川化学工業(株)製) を対パルプ 0.5%, カチオン化澱粉 0.55%, 硫酸バンド 0.8%, リテンションエイド (ハイモロック DR 3015, ハイモ(株)製) 100 ppm を各々添加し、60 g/m² の手抄きシートを調製した。

次に澱粉, 表面サイズ剤, およびクエン酸ナトリウムを固形分比が 1.5:0.2:0~0.6 のサイズプレス液を用意し、この手抄シートに対しクエン酸ナトリウム添加率が 0~0.6 g/m² となるようにサイズプレスした。これらの手抄きシートを、恒温恒湿槽にて加湿加熱処理 (JIS P 8154-3:2008, 24 h 処理) し、処理後の Δb^* からパルプの褪色抑制効果を評価した。

2.5.2 紙質への影響調査

澱粉, 表面サイズ剤, およびクエン酸ナトリウムを固形分比が 1.5:0.2:0~0.6 のサイズプレス液を用意し、工

Fig. 1 Relationship between treatment time and yellowing under various conditions of the accelerated aging tests.

場製の無サイズ紙 (米坪 59.1 g/m²) に対し, クエン酸ナトリウムの添加量が 0, 0.25, 0.5 g/m² となるようにサイズプレスし, 乾燥, 調湿後, JIS 法に従い, 紙質試験を行った。

3. 結果と考察

3.1 HexA の褪色の特徴

第一報にて報告したように, HexA 由来の褪色は高温高湿下で起こりやすいのが特徴であり, 温度と湿度がその褪色機構に影響していることが考えられる。そこで, まず, HexA 由来の褪色に及ぼす温度と湿度の影響について調査した。その結果を図 1 に示す。

図 1 は, 高 HexA 含有 LBKP を酸性抄紙した後, ①80℃, 加湿なし, ②105℃, 加湿なし, ③80℃, 相対湿度 65% に加湿, のそれぞれ 3 条件で加速褪色させた結果を示す。なお, HexA に由来する褪色は黄味が強いのが特徴であることから, 褪色の度合いは黄味の度合い, つまり, 加速褪色前後の Δb^* 値を指標として用いている。

図 1 から明らかなように, 加湿せずに加熱した場合に

は, 80℃, 105℃ で到達する値は異なるものの, Δb^* 値は共に経時的に増加した後, 平衡に達する。一方, 加湿しながら加熱した場合には, 時間と共に Δb^* 値が増加し続けることがわかる。ここで, 80℃ の条件下での褪色挙動に着目してみると, 褪色初期の段階では加湿の有無で Δb^* 値に大差はないが, ある時点から急速に差が開くことから, 少なくとも HexA の褪色反応には熱の影響を強く受ける初期反応と水の影響を強く受ける後期反応の少なくとも二段階の反応があると推測される。

これまでに, HexA に由来する褪色は紙面 pH が酸性領域で起きやすく, 褪色前後でシート中の HexA 量が減少すること¹¹⁾, HexA は酸性加熱条件下で酸加水分解すること¹⁴⁾が知られており, 上記の結果も合わせると, 褪色の初期反応は HexA の酸加水分解であり, 後期反応は前記酸加水分解物の二次反応と推測された。なお, 図 1 の①80℃, 加湿なし, ②105℃, 加湿なし条件でも褪色は起きているが, これはシート中の含有水が関与して褪色反応が起こったものと推測される。

3.2 HexA の褪色機構の推定

3.2.1 初期反応

HexA が酸加水分解すると, 二種のフラン化合物, 2-furancarboxylic acid (FA) と 5-formyl-2-furancarboxylic acid (FFA) が生成し¹¹⁾, HexA が保持していた鉄やマンガンが遊離する¹²⁾ことが知られている。これらの知見を基に, まず, HexA の分解物による褪色への影響について調査した。

図 2 は, FA, FFA, 塩化鉄 (Fe (II)), 硫化鉄 (Fe (III)), 燐酸マンガン (Mn (II)), 酢酸マンガン (Mn (III)) をそれぞれ単独, あるいは組み合わせて濾紙に添加し, Δb^* 値を測定した結果を示す。図 2 から明らかなように, FA 自体はほとんど黄味がないが, Fe (III) が共存すると著しく黄味が強まる。一方, FFA はそれ自体に弱い黄味を持つが, 鉄やマンガンを共存させても黄味は強まらない。これらの結果から, 褪色の初期段階は, HexA の酸加水分解で生成する FA と遊離する Fe (III) による呈色反応の影響が強いことが示唆された。

3.2.2 後期反応

次に, 褪色の後期反応は HexA の分解物である FA,

Fig. 2 Change of b values of the filter papers with adding the model compounds of HexA derivatives and the metals.

Fig. 3 Yellowing (80°C, 65% RH, 24 H) of the filter paper containing the model compounds of HexA derivatives and the metals.

FFA の二次反応と推定し、図 2 で使用した各サンプルを加湿加熱処理し、 Δb^* 値への影響を調査した。その結果を図 3 に示す。

加湿加熱処理した結果、FFA 単独あるいは FFA と FA、あるいは FFA と金属イオンとの組み合わせのものが著しく黄味が強まり、後期反応は主として FFA が関与することが示唆された。褪色した紙からの抽出物として、FA の存在は確認されるものの、FFA は確認されない¹²⁾との報告もあり、上記を裏付けるものと考えられる。なお、FA と Fe (III) による Δb^* 値は、加湿加熱処理により逆に低減したが、Fe (III) はパルプ中でセルロースを酸化して Fe (II) となると言われており¹¹⁾、その影響と思われた。

3.3 褪色反応へのパルプ成分の関与

3.3.1 パルプ中の多糖の関与

前述したように、HexA 由来の褪色は、HexA の酸加水分解が発端となり、さらに分解物である FFA が二次反応して進むと推測された。ここで、FFA の二次反応の相手は FFA 自身と FA だけなのか、それともパルプ中の HexA 以外の多糖成分も反応相手になるのかについて調査するため、今まで反応媒体として使用していた濾紙を針葉樹晒クラフトパルプ (NBKP) シートに換えて、3.2 と同様に FFA を添加し、加湿加熱処理を行ない、調査した。その結果を図 4 に示す。

図 4 から、FFA を濾紙に添加するよりも NBKP シートに添加した方が Δb^* 値が高くなることがわかる。このことより、FFA は NBKP 中の多糖成分とも二次反応し、さらに褪色が進むことが示唆される。

3.3.2 中性糖の関与

FFA と反応する多糖成分を明らかにすることを目的として、まず、パルプ中で含有量の多い中性糖の可能性について調査した。その結果を図 5 に示す。

図 5 は、中性糖としてグルコース、キシロース、マンノースを選び、酸性濾紙に FFA と共に添加し、加湿加熱処理した結果を示す。図 5 から、FFA は中性糖とは反応せず、また中性糖自身も褪色に関与しないことが明らかとなった。

3.3.3 酸性糖の関与

次に酸性糖の関与の可能性について調査した。その結果

Fig. 4 Yellowing of FFA on filter paper or handsheet made from NBKP after ageing.

Fig. 5 Yellowing of FFA and neutral sugars on filter paper after ageing.

を図 6 に示す。

図 6 は、酸性糖としてグルクロン酸、ガラクトン酸を選び、酸性濾紙に FFA と共に添加し、加湿加熱処理した結果である。図 6 から、FFA は酸性糖とも反応し、褪色

Fig. 6 Yellowing of FFA and uronic acids on filter paper after ageing.

がより強まることが明らかとなった。また、酸性糖自身も褪色反応を引き起こすことがわかった。

3.4 HexA の褪色機構の総括

以上の結果から、HexA に由来するパルプの褪色は、まず HexA が酸加水分解して二種のフラン化合物、2-furancarboxylic acid (FA) と 5-formyl-2-furancarboxylic acid (FFA) を生成し、さらに FFA 自身、あるいは FFA と FA、FFA とパルプ中の酸性糖が二次反応して起こると推測さ

れた。

3.5 褪色抑制剤の探索

3.5.1 低分子ポリカルボン酸

前記 HexA に由来するパルプの褪色機構から、FFA による二次反応を止められれば、HexA が存在していても褪色を抑えることができると考えられる。FFA は FA あるいは酸性糖と反応することが示されたので、カルボキシル基を有する化合物と反応する可能性が高いと考え、カルボキシル基を有する化合物の中から褪色抑制効果のあるものを探索することとした。まず、比較的入手の容易な 10 種の低分子カルボン酸（構造式は図 7 を参照）について調査した。その結果を図 8 に示す。

図 8 は、高 HexA 含有パルプを用いてラボで調製したシートに低分子カルボン酸を添加した後、加湿加熱処理し、その前後の Δb^* を示している。無添加のものに対して、グリコール酸と乳酸以外の低分子カルボン酸を添加したシートの Δb^* は小さくなり、褪色抑制の効果があることがわかる。また、クエン酸ナトリウムのようなカルボン酸の塩を用いた場合でも、褪色抑制の効果が確認された。グルコン酸のような例外はあるものの、一分子中にカルボキシル基を複数持つポリカルボン酸に褪色抑制効果があることがわかった。

また、低分子ポリカルボン酸の添加率と褪色抑制効果の関係を調べるために、クエン酸と酒石酸を用い、添加率を変えて同様の実験を行なった（図 9）。その結果、添加率を 0.1% まで下げても十分な褪色抑制効果が得られ、実用

Fig. 7 Chemical formula of low molecular weight carboxylic acids

Fig.8 Effect of low molecular weight carboxylic acids on depressing the yellowing

Fig.9 Effect of charge of citric acid and tartaric acid on depressing the yellowing

Fig.10 Effect of PAA on depressing the yellowing
*The number after PAA means average molecular weight of PAA.

的であることが確認された。

3.5.2 高分子ポリカルボン酸

次に、高分子のポリカルボン酸についても調査した。高分子のポリカルボン酸としては、既に内添薬品と知られているポリアクリル酸 (PAA) を用い、その褪色抑制効果を前述と同様の方法で調べた。その結果を図 10 に示す。

分子量の異なる 3 種の PAA について調査したが、褪色抑制の効果はあるものの、その効果はクエン酸のような低分子ポリカルボン酸よりも小さかった。これは、低分子ポリカルボン酸の方が、同一添加率ではカルボキシル基量が多くて反応場が多いことと、分散性が良く、パルプに対し均一に添加できたためと思われる。

3.6 低分子ポリカルボン酸外添による褪色抑制

クエン酸のようなポリカルボン酸を紙に添加する方法として、内添法と外添法があるが、内添法についてはパルプへの定着が困難であり、また、添加量も多く必要で現実的ではないと判断し、外添法について詳細に検討した。

まず、低分子ポリカルボン酸としてクエン酸を用い、サイズプレスによる外添法について検討したが、サイズプレ

ス液に含まれるサイズ剤によってはクエン酸の添加で凝集するものがあった。そのため、以後の検討ではクエン酸ナトリウムを用いることとした。

3.6.1 低分子ポリカルボン酸の必要添加量

図 11 は、高 HexA 含有パルプから成る 60 g/m^2 の手抄シートに $0 \sim 0.6 \text{ g/m}^2$ のクエン酸ナトリウムを外添した場合の褪色抑制結果を示す。図 11 に示すように、クエン酸ナトリウムの添加量が $0 \sim 0.3 \text{ g/m}^2$ の範囲では Δb^* は直線的に減少し、 0.3 g/m^2 を超えるとほぼ平衡に達した。このことから、クエン酸ナトリウムを 0.3 g/m^2 以上外添すれば、褪色を概ね抑制できると判断した。

3.6.2 低分子ポリカルボン酸外添による紙質への影響

クエン酸ナトリウムをサイズプレスにて外添した場合の紙質への影響を調査するため、サイズプレス前の工場製原紙を用い、サイズプレス時のクエン酸ナトリウム添加量を変え、それぞれの紙質を測定した。その結果を表 1 に示す。表 1 から明らかなように、クエン酸ナトリウムをサイズプレスで外添しても紙質への影響はなく、クエン酸ナトリウ

Table 1 Physical paper properties and Stöckigt sizing degree of size-pressed paper with sodium citrate

Sodium citrate g/m ²	Surface sizing agent g/m ²	Tear index (MD) mN·m ² /g	Tear index (CD) mN·m ² /g	Bleaching length (MD) Km	Bleaching length (CD) Km	Internal bond strength J/m ²	Stöckigt sizing degree s
0.00	0.20	7.9	8.8	8.5	3.5	535	28
0.25	0.20	8.8	8.8	8.1	3.6	541	29
0.50	0.20	8.5	9.5	8.2	3.5	529	27
0.50	0.35	8.3	9.2	8.4	3.5	511	26

Fig. 11 Relationship between a coating weight of sodium citrate and Δb^* of coated paper

ムのような低分子ポリカルボン酸塩の外添による褪色抑制法は実用的であることが確認された。この褪色抑制法は、パルプ中の HexA を除去することなく、サイズプレス液に低分子ポリカルボン酸塩を添加するだけで実施できるため、パルプ製造工程での大幅な省エネが可能である。

4. 結 論

ヘキセンウロン酸 (HexA) を除去することなく、無塩素漂白パルプの褪色を防止する方法を見出す手がかりを得るため、まず、HexA の褪色機構を調査した。その結果、HexA の褪色反応は少なくとも二段階の反応から成り、初期反応は HexA の酸加水分解であり、後期反応は HexA の酸加水分解物の一つである FFA の二次反応であると推測された。このうち、後期反応の FFA による二次反応は特に褪色へ寄与が大きく、FFA の二次反応を抑制できれば概ね褪色を抑制できることも示唆された。

FFA の二次反応を阻害する化合物を探索した結果、クエン酸、酒石酸、リンゴ酸、琥珀酸、グルコン酸、マロン酸、イタコン酸といった低分子ポリカルボン酸やその塩、

あるいは PAA のような高分子ポリカルボン酸に褪色抑制効果が認められた。これらのポリカルボン酸を添加する方法としては、ポリカルボン酸の塩をサイズプレスにより外添する方法が適しており、紙質に影響を与えることなく、褪色を抑制することができた。

References

- 1) A. Kawae and Y. Uchida : JAPAN TAPPI J. in press
- 2) T. Kobayashi, A. Lindström and M. Wennerström : JAPAN TAPPI J. 59 (4) 483-489
- 3) T. Vourinen, A. Teleman and P. Fagerström : International Pulp Bleaching Conference Proceedings, Washington, D. C., 43-51 (1996)
- 4) M. Siltala, K. Winberg and B. Lonnberg : International Pulp Bleaching Conference Proceedings, Helsinki, 279-287 (1998)
- 5) D. Lachenal and C. Chirat : Pulping Conference Proceedings, Montreal, TAPPI PRESS, 601-604 (1998)
- 6) M. Wennerström : International Pulp Bleaching Conference Proceedings, Portland, 265-278 (2002)
- 7) H. Ohi : JAPAN TAPPI J. 60 (11) 1659-1663 (2006)
- 8) M. Ragner : 11 th International Symposium on Wood and Pulping Chemistry Proceedings Vol. 3, Nice, 363-366 (2001)
- 9) F. P. Furtado, D. V. Evtugin and T. M. Gomes : Pulp Paper Canada 102 (12) 89-92 (2001)
- 10) K. M. M. Eiras and J. L. Colodette : J. Pulp Paper Science 29 (2) 64-69 (2003)
- 11) A. Granström, C. Rööst and G. Gellerstedt : Nordic Pulp Paper Research J. 16 (1) 18-23 (2001)
- 12) A. Granström, and G. Gellerstedt : Nordic Pulp Paper Research J. 17 (4) 427-433 (2002)
- 13) A. Kawae and Y. Uchida : APPITA J. 58 (5) 378-381 (2005)
- 14) B. Lindberg, J. Lönnren and J. L. Thompson : Carbohydrate Research 28, 351-357 (1973)

(受理: '09.11.11)

JAPAN TAPPI JOURNAL accepts scientific papers written either in Japanese or in English. We, JAPAN TAPPI, translate them into the other of the two languages (Japanese into English and English into Japanese) and print them in addition to the originals under the permission of the authors. We believe that this service of translation will help our subscribers to find and understand the scientific value of the original paper more clearly, and will contribute to the development of science and technology in the paper industry.

- Regarding figures and tables, refer to the original article in Japanese.
- The copy right of the translated version belongs to JAPAN TAPPI.
- If there is any inconsistency between the two versions, the original is always true.
- JAPAN TAPPI is not responsible to any outcomes based on the translated version.

1. Introduction

The bleaching process of kraft pulp was converted from conventional one using chlorine to chlorine free processes like ECF bleaching and TCF bleaching since the 1990 s. Then, yellowing became occasionally troublesome in paper containing pulp bleached by chlorine free processes, and paper manufactured by acidic sheet forming was more frequently troubled. The reason of the yellowing was studied mostly in the North European countries with bleached softwood pulp (NBKP) of which brightness was about 90% ISO. It is now understood as true that hexenuronic acid (HexA) was influential. As pulp most commonly used in Japan is bleached hardwood pulp of which brightness is about 86% ISO, we studied the yellowing of that pulp and reported in our first paper that HexA was also influential, especially under a humid and hot condition. We also studied the influence of bleaching sequences and reported in our first paper that ECF pulp bleached mostly by chlorine dioxide tended to have more amount of residual HexA, and was less stable in brightness. The reason was that chlorine dioxide progressed delignification more favorably than decomposition of HexA, which tended to be remaining. To cope with that, Kappa number of unbleached pulp should be controlled to one at which the ratio of HexA against lignin (HexA/lignin) in pulp could be as low as possible¹⁾.

Conventional counter measure is to remove HexA by treatments like acid treatment, chlorine dioxide treatment of high temperature and ozone treatment at high charge rate²⁻⁷⁾. They have unfavorable side effects such as pulp yield is reduced, pulp strength is lost and refinability is worsened⁸⁻¹⁰⁾. Therefore, a process is wanted which improves brightness reversion without removing HexA. We investigated the mechanism of yellowing caused by HexA, and found the process that satisfied what was wanted.

2. Experiment

2.1 Preparation of LBKP of high HexA content and yellowing test

LBKP of high HexA content was prepared from hardwood kraft pulp after oxygen delignification manufactured

in mill (brightness : 55% ISO, Kappa number : 9.3) by bleaching it with D 0-E-P-D 1 sequence. Its brightness was 83.5% ISO and its HexA content was 17.6 mmol/kg. Hand sheets were prepared from the LBKP under an acidic condition (pH 4.5), and were tested for yellowing. The yellowing was carried out at three conditions, 80°C without humidity control, 105°C without humidity control and 80°C at 65% R. H. Test sheet was taken out from a conditioned chamber after different holding times, 3 hours, 10 hours, 24 hours and 48 hours respectively, and its chromaticity b^* (ISO 5631-2000) was measured. Δb^* which was the difference between b^* s before and after yellowing was an indicator for brightness reversion or yellowing.

2.2 Yellowing test with model chemicals (Part 1)

Filter paper (Advantec No. 2) available in the market was immersed in sulfuric acid solution of which concentration was 0.1 mmol/L, and then was dried in air to get acidified filter paper of which surface pH was 4.5 and of which weight was 1 g BD/sheet. The acidified filter paper was treated with following chemicals, and dried under the humid and hot condition for 24 hours (JIS P 8154-3 : 2008). Δb^* was calculated from the difference between b^* s before and after the treatment.

(Trial 1)

- 2-furancarboxylic acid (FA) : 45.5 μ mol
- 5-formyl-2-furancarboxylic acid (FFA) : 4.5 μ mol
- Ferrous chloride (II), Ferric sulfate (III) 4.5 μ mol
- Manganese phosphate (II), Manganese acetate (III) : 35 μ g

(Trial 2)

- 5-formyl-2-furancarboxylic acid (FFA) : 10 μ mol
- Glucose, xylose, mannose : 10 μ mol respectively

(Trial 3)

- 5-formyl-2-furancarboxylic acid (FFA) : 10 μ mol
- Glucronic acid, galactronic acid : 10 μ mol respectively
(by Wako Pure Chemical Industries, Ltd.)

2.3 Yellowing test with model chemicals (Part 2)

1 g BD of bleached softwood kraft pulp (NBKP) was sheeted by hand sheet former under an acidic condition to get an acidified hand sheet of which surface pH was 4.5. 10 μ mol of FFA was added to the hand sheet, which was dried under the humid and hot condition (JIS P 8154-

3 : 2008) for 24 hours. Δb^* was calculated from the difference between b^* s before and after the treatment.

2.4 Screening test for inhibitors to yellowing

2.4.1 Carboxylic acids of low molecular weight

LBKP of high HexA content was prepared from hardwood kraft pulp after oxygen delignification manufactured in mill (LOKP) (brightness : 55% ISO, Kappa number : 9.3) by bleaching it with D 0-E-P-D 1 sequence in lab. Hand sheets were prepared from that LBKP under the acidic condition (JISP 8222 : 1908). The hand sheets were impregnated with 10 kinds of carboxylic acids of low molecular weight respectively, (citric acid, tartaric acid, malic acid, succinic acid, glycolic acid, lactic acid, gluconic acid, malonic acid, itaconic acid and sodium tatarate from Wako Pure Chemicals), at the charge rate of 5% based on pulp, and dried in air. The hand sheets were kept under the hot and humid condition (JIS P 8154-3-2008) for 24 hours in a controlled chamber. After the treatment, Δb^* was calculated for evaluating the effect of inhibiting yellowing. Regarding citric acid and tartaric acid, three levels of charge rates, 0.1%, 0.5% and 1%, were tested in the same way.

2.4.2 Carboxylic acids of high molecular weight

Three poly-acrylic acids of different molecular weights (average molecular weight : 5,000, 25,000 and 250,000 respectively supplied by Wako Pure Chemical industries, Ltd.), instead of 10 carboxylic acids, were added at the rate of 0.5% respectively, following the procedures in 2.4.1. The effect of suppressing brightness reversion or yellowing was studied.

2.5 Surface sizing with sodium citrate

2.5.1 The effect of sodium citrate added to sheet

LBKP of high HexA content was beaten in a Niagara beater. After rosin size (SPYA 50 by Arakawa Chemical Industries, Ltd.), cationic starch, aluminum sulfate and retention aid (Hymolock DR 3015 by Hymo Co., Ltd.) were added to it at the rate of 0.5%, 0.55%, 0.8% and 100 ppm respectively, the pulp was formed to hand sheets of which basis weight was 60 g/m².

Surface sizing liquor was prepared which consisted of starch, surface sizing agent and sodium citrate at the ratio of 1.5 : 0.2 : 0-0.6 among them in solid basis. The hand sheet was surface sized with the liquor so that the sheet had sodium citrate at the charge rate from zero to 0.6 g/m² in it. The sheet was kept under the hot and humid condition (JIS P 8154-3-2008) for 24 hours in a controlled chamber. After the treatment, Δb^* was calculated for evaluating the effect of suppressing yellowing.

2.5.2 The effect on sheet quality

Surface sizing liquor was prepared which consisted of starch, surface sizing agent and sodium citrate at the ratio of 1.5 : 0.2 : 0-0.6 among them in solid basis. Paper manufactured in mill without sizing of which basis weight

was 59.1 g/m² was surface sized with the liquor so that the paper had sodium citrate at the different charge rates, zero, 0.25 and 0.5 g/m² respectively in it. After dried and conditioned according to JIS, its paper quality was measured.

3. Result and discussion

3.1 The characteristics of yellowing caused by HexA

The brightness reversion or yellowing by HexA tended to occur in a humid and hot condition, as we reported in our first paper. As temperature and humidity were supposed to be influential, their influences were studied in our first step.

Fig. 1 summarizes yellowing in three accelerated aging conditions, 80°C without humidification, 105°C without humidification and 80°C at 65% R. H., with hand sheets prepared from LBKP of high HexA content by acidic sheet forming. As yellowing caused by HexA was yellowish in color, the degree of yellowing was represented by Δb^* which was difference in b^* s before and after accelerated aging tests.

In the conditions without humidification, their Δb^* s increased along with aging time and then got saturated, though their values were not the same. On the other hand, Δb^* kept increasing with aging time in the humid condition. When the case was more closely compared with one under 80°C without humidification, they behaved almost in the same way at the early stage, and they diverged after that. It suggested that yellowing by HexA proceeded at least in two reactions, one which was at an early stage and was affected with temperature and one which was at a later stage and was affected with humidity or water.

It is known that yellowing by HexA occurred when surface pH of sheet turned to acidic and the content of HexA in sheet got reduced after yellowing¹¹⁾. HexA itself was hydrolyzed in an acidic condition under heat¹⁴⁾. So, it was reasoned that the reaction at the early stage of yellowing was hydrolysis of HexA and that in the late stage was subsequent reaction by hydrolyzed products from HexA. It was true that yellowing occurred in the two cases without humidification. It was assumed that water in sheets helped initiating yellowing.

3.2 The mechanism of yellowing by HexA

3.2.1 Yellowing in the early stage

When HexA is hydrolyzed, two kinds of furan compounds, 2-furancarboxylic acid (FA) and 5-formyl-2-furancarboxylic acid (FFA), are produced¹¹⁾, and manganese and iron ions which have been retained by HexA are released¹²⁾. How those decomposed products from HexA affected on yellowing was investigated.

FA, FFA, ferrous chloride (Fe (II)), ferric sulfate (Fe (III)), manganese phosphate (Mn (II)) and manganese

acetate (Mn (III)) were added to filter paper, individually and in some cases as their mixture, and Δb^* values were measured. The results are summarized in Fig. 2. FA under the presence of Fe (III) increased yellowness, though it was not yellowish by itself. On the other hand, FFA which was slightly yellowish did not enhance its yellowness under the presence of iron and manganese ions. It was suggested that the yellowing at the early stage was caused by interaction between FA, which was a hydrolytic product of HexA, and Fe (III) which was released from HexA.

3.2.2 Yellowing in the late stage

We assumed that the yellowing in the late stage was a subsequent reaction by FA and FFA hydrolyzed from HexA. Samples prepared for Fig. 2 were treated under the hot and humid condition and their Δb^* values were measured. The result is in Fig. 3.

The fact that samples with FFA alone, FFA with FA and FFA with metals turned to strongly yellowish suggested that FFA took significant share in the yellowing in the late stage. It was reported that FA was existent in extractive from pulp after yellowing and FFA was not existent¹²⁾, which also supported our reasoning. In a case of FA with Fe (III), the humid and hot treatment decreased its Δb^* value. It is said that Fe (III) oxidizes cellulose in pulp and turns to Fe (II), and it might be influential in the case.

3.3 Participation of components in pulp to yellowing

3.3.1 Oligosaccharides in pulp

It was assumed from our early study that yellowing by HexA was initiated by hydrolysis of HexA and then FFA, which was a decomposed product, led to the subsequent reaction. Then, our interest was whether only FFA was responsible to the subsequent reaction or some oligosaccharides took part in the reaction. So, we changed filter paper to softwood bleached kraft pulp (NBKP) sheet, and followed the procedures in 3.2 with FFA being added. After treated under the humid and hot condition, the result is summarized in Fig. 4.

NBKP sheets with FFA being added gave larger Δb^* value than filter paper with FFA as in Fig. 4. It suggested that FFA with help from oligosaccharides in NBKP sheet put forward the subsequent reaction further.

3.3.2 Neutral sugar

To make clear what oligosaccharides reacted with FFA, neutral sugar which were rich in pulp were taken for study. The result is in Fig. 5.

Glucose, xylose and mannose were selected, and they were added to acidic filter paper along with FFA. After treated under the humid and hot condition, Δb^* values were measured. It became clear that neutral sugars did not react with FFA and did not take part in the reaction.

3.3.3 Acidic sugar

Our next subject was acidic sugars. The result is in Fig. 6.

Glucuronic acid and galacturonic acid were selected, and they were added to acidic filter paper along with FFA. After treated under the humid and hot condition, Δb^* values were measured. It turned out that FFA reacted with acidic sugars and enhanced yellowing. Acidic sugars themselves initiated yellowing.

3.4 The mechanism of yellowing by HexA

In summary, yellowing of pulp by HexA progressed as follows. HexA was hydrolyzed to two kinds of furans, 2-furancarboxylic acid (FA) and 5-formyl-2-furancarboxylic acid (FFA). Then, FFA reacted with FFA itself, with FA and with acidic sugars in pulp in the subsequent reaction.

3.5 Inhibitors to yellowing

3.5.1 Poly-carboxylic acid of low molecular weight

Inferring from the mechanism of yellowing, yellowing would be suppressed even in the presence of HexA if the subsequent reaction by FFA was inhibited. As FFA was found to react with FA or acidic sugars, and would react with chemicals having carboxylic group in them, those compounds would be able to work as inhibitors to yellowing. Firstly, ten carboxylic acids of low molecular weight that were easily available were tested. Their configurations are in Fig. 7 and the result is in Fig. 8.

Hand sheets were prepared from pulp of high HexA content mentioned before, to which carboxylic acid was added. After treated under the humid and hot condition, Δb^* values were measured. The carboxylic acids except glycolic acid and lactic acid reduced Δb^* values, compared with the blank test, and were thought to be effective inhibitors. Sodium citrate, a salt of carboxylic acid, was also found to be effective. Poly-carboxylic acids which had more than one carboxylic group in them were also effective against yellowing, though there was an exception like gluconic acid.

The relationship between the charge rate of carboxylic acid of low molecular weight and its effectiveness as an inhibitor was studied with citric acid and tartaric acid at different charge rates (refer to Fig. 9). Even the charge rate of 0.1% worked well and the method was demonstrated to be practical.

3.5.2 Poly-carboxylic acid of high molecular weight

Our next subject was poly-carboxylic acid of high molecular weight. We took poly-acrylic acid (PAA), a well known additive in paper making, and investigated its effect on suppressing yellowing in the procedure described before. The result is in Fig. 10.

Three PAAs which had different molecular weights were tested. Though they were effective, they worked

less than poly-carboxylic acid of low molecular weight like citric acid. The reason would be that poly-carboxylic acid of low molecular weight had a larger number of carboxylic group based on the same charge rate, could be well dispersed, and could be more evenly added to pulp.

3.6 Surface sizing with low molecular poly-carboxylic acid

There are two methods for adding poly-carboxylic acid like citric acid to paper, wet end addition and surface sizing. We thought that wet end addition was not practical, as the chemical would be rarely retained to pulp and its charge rate would be large. So, we took surface sizing as our process.

We found that some surface sizing agents got coagulated by citric acid. Therefore, we used sodium citrate instead.

3.6.1 Necessary charge rate of low molecular weight poly-carboxylic acid

Sodium citrate was added by surface sizing to hand sheet which consisted of pulp that had HexA at high content. The basis weight of hand sheet was 60 g/m² and the charge rate was from zero to 0.6 g/m². As in Fig. 11, Δb^* decreased lineally by increasing the charge rate up to 0.3 g/m², and then got saturated. It was suggested that yellowing could be suppressed by surface sizing paper with sodium citrate at the charge rate more than 0.3 g/m².

3.6.2 Influence on sheet quality by surface sizing with low molecular weight poly-carboxylic acid

In order to study how surface sizing with low molecular weight carboxylic acid affected on sheet quality, paper was taken out before size press in a mill and was surface sized with sodium citrate at different charge rates. The sheet qualities are summarized in Table 1. It was verified that surface sizing with sodium citrate did not deteriorate sheet quality and the method was practical for suppressing yellowing. As the method does not ask to remove HexA existent in pulp, large energy saving will be expected in pulping operation.

4. Conclusion

To find the method of suppressing yellowing of bleached pulp by chlorine free processes without removing HexA, the mechanism of yellowing was investigated. It was found that yellowing by HexA went through at least two reaction stages, and the early stage was hydrolysis of

HexA and the late stage was subsequent reaction by FFA which was a hydrolytic product of HexA. As the subsequent reaction by FFA in the later stage was most influential to yellowing, it was suggested that suppressing the subsequent reaction would work for suppressing yellowing.

We looked for compounds which could suppress the subsequent reaction, and found that poly-carboxylic acids of low molecular weight, like citric acid, tartaric acid, malic acid, succinic acid, gluconic acid, malonic acid, itaconic acid and their salts, and high molecular weight poly-carboxylic acid like PAA could effectively work. As for the process of adding these poly-carboxylic acids to paper, surface sizing with their salts was practical and could suppress yellowing without deteriorating sheet quality.

References

- 1) A. Kawae and Y. Uchida : JAPAN TAPPI J. in press
- 2) T. Kobayashi, A. Lindström and M. Wennerström : JAPAN TAPPI J. 59 (4) 483-489
- 3) T. Vourinen, A. Teleman and P. Fagerström : International Pulp Bleaching Conference Proceedings, Washington, D. C., 43-51 (1996)
- 4) M. Siltala, K. Winberg and B. Lonnberg : International Pulp Bleaching Conference Proceedings, Helsinki, 279-287 (1998)
- 5) D. Lachenal and C. Chirat : Pulping Conference Proceedings, Montreal, TAPPI PRESS, 601-604 (1998)
- 6) M. Wennerström : International Pulp Bleaching Conference Proceedings, Portland, 265-278 (2002)
- 7) H. Ohi : JAPAN TAPPI J. 60 (11) 1659-1663 (2006)
- 8) M. Ragner : 11 th International Symposium on Wood and Pulping Chemistry Proceedings Vol. 3, Nice, 363-366 (2001)
- 9) F. P. Furtado, D. V. Evtugin and T. M. Gomes : Pulp Paper Canada 102 (12) 89-92 (2001)
- 10) K. M. M. Eiras and J. L. Colodette : J. Pulp Paper Science 29 (2) 64-69 (2003)
- 11) A. Granström, C. Röst and G. Gellerstedt : Nordic Pulp Paper Research J. 16 (1) 18-23 (2001)
- 12) A. Granström, and G. Gellerstedt, : Nordic Pulp Paper Research J. 17 (4) 427-433 (2002)
- 13) A. Kawae and Y. Uchida : APPITA J. 58 (5) 378-381 (2005)
- 14) B. Lindberg, J. Lönnren and J. L. Thompson : Carbohydrate Research 28, 351-357 (1973)