

## Kraft mill bleach plant effluents: recent developments aimed at decreasing their environmental impact, part 1

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*A clear-cut relationship between the release of chlorinated organic material and biological and ecological effects in the receiving waters has not yet been established.*

Recently, there has been increasing concern within the pulp and paper industry about the environmental impact of chemical compounds created in the pulping and bleaching process. These compounds are not completely decomposed in the conventional wastewater treatment processes; subsequently, they enter the environment via the mills' discharges. Scientific studies are incomplete, and debate continues as to whether these compounds represent any true risk to the environment. Nevertheless, many advances have been made in pulping and bleaching technology through work designed to minimize the formation of chemical compounds believed to be deleterious to the environment.

In particular, chemical compounds that contain chlorine have been identified as the major source of concern. These are generally referred to collectively as "chlorinated organics" and include all varieties of chlorinated organic materials, regardless of molecular weight, including 2,3,7,8-tetrachlorodibenzo-*p*-dioxin, which is also known as "TCDD," or simply as "dioxin." Conventional pulp bleaching, which includes chlorination, will typically produce 15-20 lb of chlorinated organic materials per ton of bleached pulp prior to effluent treatment.

Our object here is not to examine whether chlorinated organic materials do indeed pose a risk to the environment. Instead, we offer a review of developments in the technology of pulping and bleaching that have demonstrat-

ed new ways to decrease the formation of chlorinated organic materials. Our review also includes a look at the composition of bleach plant effluent and at the effluent treatment methods that have been studied as ways to remove chlorinated organic materials from the discharge.

### Bleach plant effluent characteristics

Conventional bleaching of chemical pulp involves the use of (a) chlorine and chlorine dioxide in the first stage, known as the chlorination or C stage, and (b) caustic soda extraction, with or without oxygen, in the second stage, known as the extraction or E stage. Oxidation by chlorine and chlorine dioxide and substitution of chlorine into the molecular structure of the residual lignin in the pulp occur in the first stage, generating many species of chlorinated organic compounds.

The highest concentration of chlorinated material occurs in the chlorination and extraction effluents, and the chemical and biological characterization of these effluents has been extensively studied. Recently, the total organically-bound chloride (TOCl) measurement has been proposed by Swedish environmental authorities as a monitoring and pollution control parameter.

The TOCl test involves extensive sample preparation after a one-week storage period and was designed originally as a research tool. In the analysis of effluents from bleaching stages, the aim of this test is to account for all of the chlorine that has reacted with lignin to form chlorinated organic material. It does not measure highly volatile chlorinated organics such as chloroform. More recently, the AOX (adsorbable organic halide) test has also been considered as a regulatory guideline. This test involves no storage of liquor, it is not specific for chlorine, but it does encompass any halide—fluoride, chloride,

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bromide, or iodide. Generally, it gives a higher absolute value than the TOCl test.

Several specific terms are used to describe the characteristics of bleach plant effluents. Effluents are characterized by their BOD, COD, mutagenicity, color, and acute and chronic toxicity. BOD and COD stand for biological oxygen demand and chemical oxygen demand, respectively. Both of these parameters relate to the amount of oxygen required in the receiving water to react with the effluent. Mutagenicity is a measure of the ability of the effluent to induce genetic mutation and is commonly measured with the Ames test. Toxicity is defined as an adverse effect caused by the effluents to a test organism, typically fish or invertebrates, over a specific period and at a particular concentration of the effluent. Acute toxicity is defined as the effects occurring within a short time period, such as 24-96 h. Chronic toxicity characterizes the long-term effects of exposure to the effluent and examines growth, metabolism, and reproductive ability.

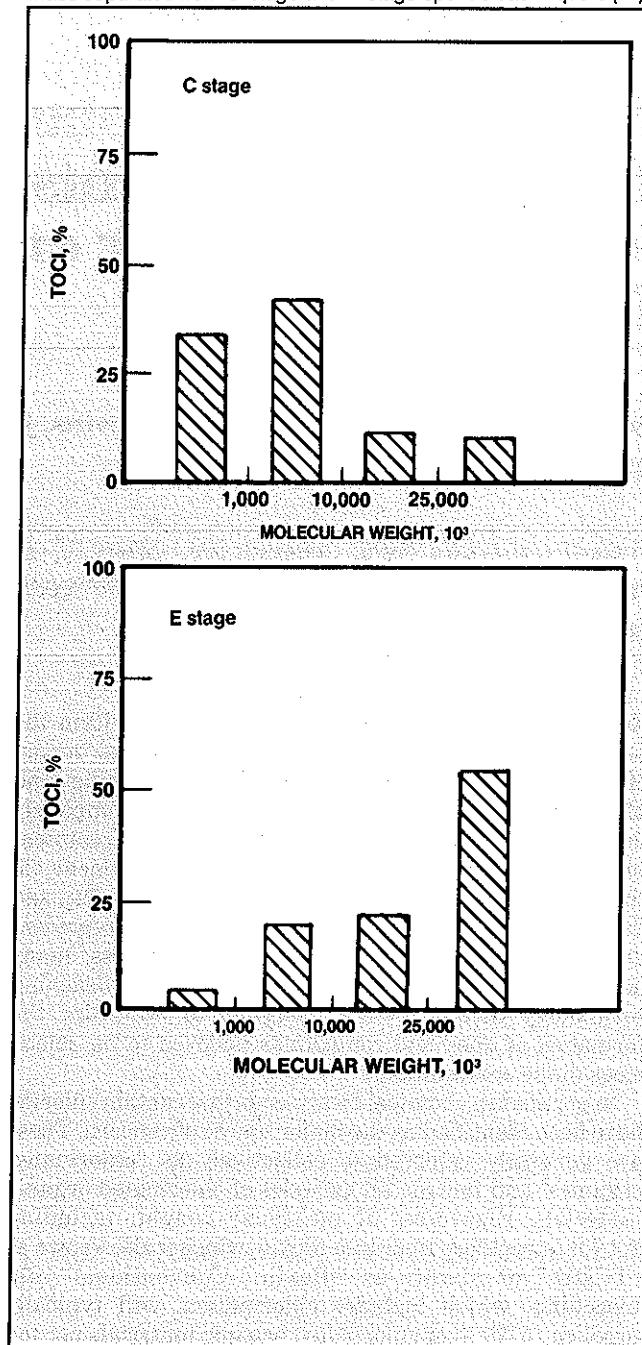
Bleach plant effluents usually exhibit acute toxicity and some mutagenic activity (1-8). Resin and fatty acids and chlorinated phenolics are the principal contributors to effluent toxicity (3-7). High concentrations of resin acid cause much of the toxicity to aquatic organisms of combined effluents (3-5). Low-molecular-weight, chlorinated, neutral compounds are major contributors to mutagenicity (2). The dominant chlorophenolics in C-stage effluent are chlorocatechols, whereas chloroguaiacols are the major species in E-stage effluent.

The chlorinated phenolics are major contributors to effluent toxicity (5-7, 9). High toxicity levels have been observed when low concentrations of resin acid and chlorophenolics were present (4, 5). Furthermore, detailed analyses of individual toxic components of bleach plant effluents have shown repeatedly that it is difficult to predict the toxicity by calculating the toxic contributions of these compounds (4-6, 9, 10, 11). Competitive or synergistic effects are caused by mixing effluents or individual components, and important contributors to effluent toxicity probably have not yet been identified. Mill process changes that decrease the production of chlorinated phenolics were recently shown to lead to a higher acute toxicity of the mill effluent (12).

Chlorinated phenolics represent less than 2% of the organically bound chloride in bleaching effluents. Most of the chloride is bound in high-molecular-weight chlorolignin, which is stable against biodegradation and contributes little to toxicity, mutagenicity, and BOD. Lindstrom *et al.* (13) analyzed the relative molecular weight distribution of TOCl in spent C and E liquors (Fig. 1). The liquors contained approximately 3 kg and 2 kg TOCl per metric ton of pulp, respectively. The chlorinated degradation products were identified from oxidative degradation of high-molecular-weight chlorolignin.

Resin acids, chlorinated phenolics, and other chlorinated compounds can be taken up and accumulated readily by fish and other aquatic organisms, but clearance from the body is usually rapid once exposure is curtailed (3, 14). Recent projects have begun to examine the long-term impact of the breakdown of high-molecular-weight chlorolignin.

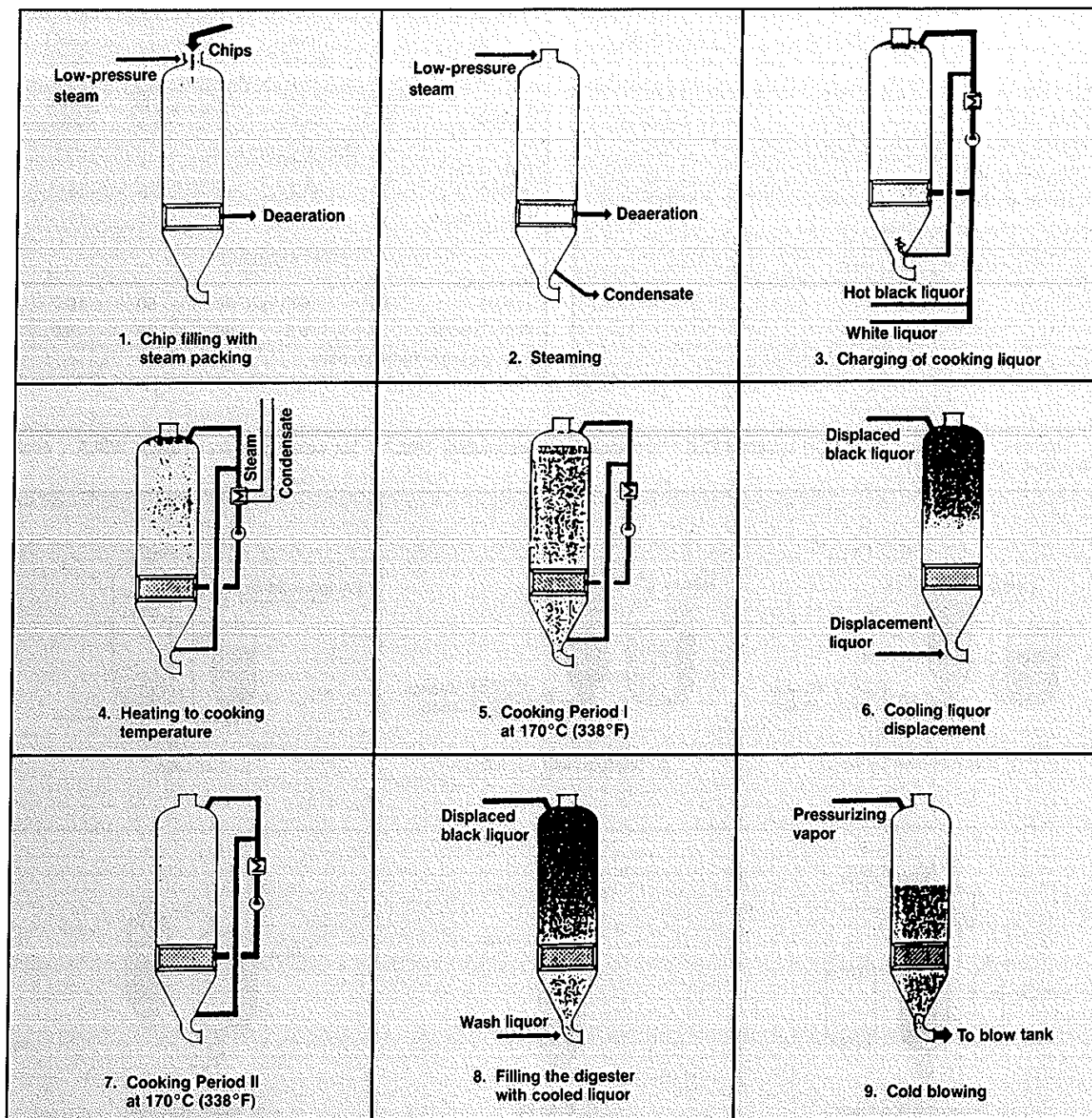
1. The distribution of TOCl in fractions of different relative molecular mass separated from C-stage and E-stage spent bleach liquors (12)



### Extended delignification

The amount of chlorinated material produced via the chlorination and extraction of pulp is a function of the amount of chlorine applied to the pulp. Axegard has shown (15-17) that the formation of chlorinated organic compounds is reduced proportionally as the amount of chlorine applied to the pulp is reduced. In the conventional chlorination of pulp, the chlorine charge is determined by the residual lignin in the pulp, which is in turn determined indirectly via oxidation with potassium permanganate to give a kappa number (or permanganate number). If the

## 2. Sunds Defibrator cold blow combined with extended delignification (21)



overall objective is to decrease the chlorine charge, a simple solution is to reduce the chlorine demand of the pulp by lowering the kappa number of the pulp prior to bleaching. One way to do this is to remove more lignin during pulping, an approach termed "extended delignification" (18, 19).

Conventional kraft pulping of softwood for a bleachable grade of pulp results in a pulp with a kappa number of 28-32. For hardwoods, the range of kappa numbers is typically 18-22. A further reduction of the kappa number during pulping could be attained by increasing the pulping time or alkali charge, but either would cause a greater

alkaline degradation of the pulp, resulting in a lower yield and poorer physical properties.

Extended delignification has overcome these problems by improving the selectivity of delignification during pulping. Sjöblom *et al.* (18, 19) have shown that improved selectivity during delignification can be achieved if three conditions are met. First, the effective alkali charge ( $\text{NaOH} + 1/2 \text{Na}_2\text{S}$ ) must be initially lowered and made more uniform during pulping. Second, the highest practical sulfidity must be maintained. Third, the concentration of dissolved lignin in the pulping liquor must be lowered during the latter part of the cook. To adapt

I. Environmental influence of effluents from bleaching of modified and conventional pulps (spent liquors from bleaching experiments)

|                              | Modified | Conventional |
|------------------------------|----------|--------------|
| Kappa no.                    | 25       | 32           |
| BOD, mg/dm <sup>3</sup>      | 480      | 675          |
| COD, mg/dm <sup>3</sup>      | 3931     | 4618         |
| TOC, mg/dm <sup>3</sup>      | 1220     | 1579         |
| TOCl, mmol/dm <sup>3</sup>   | 1.45     | 1.93         |
| Color, Pt mg/dm <sup>3</sup> | 7065     | 10,202       |

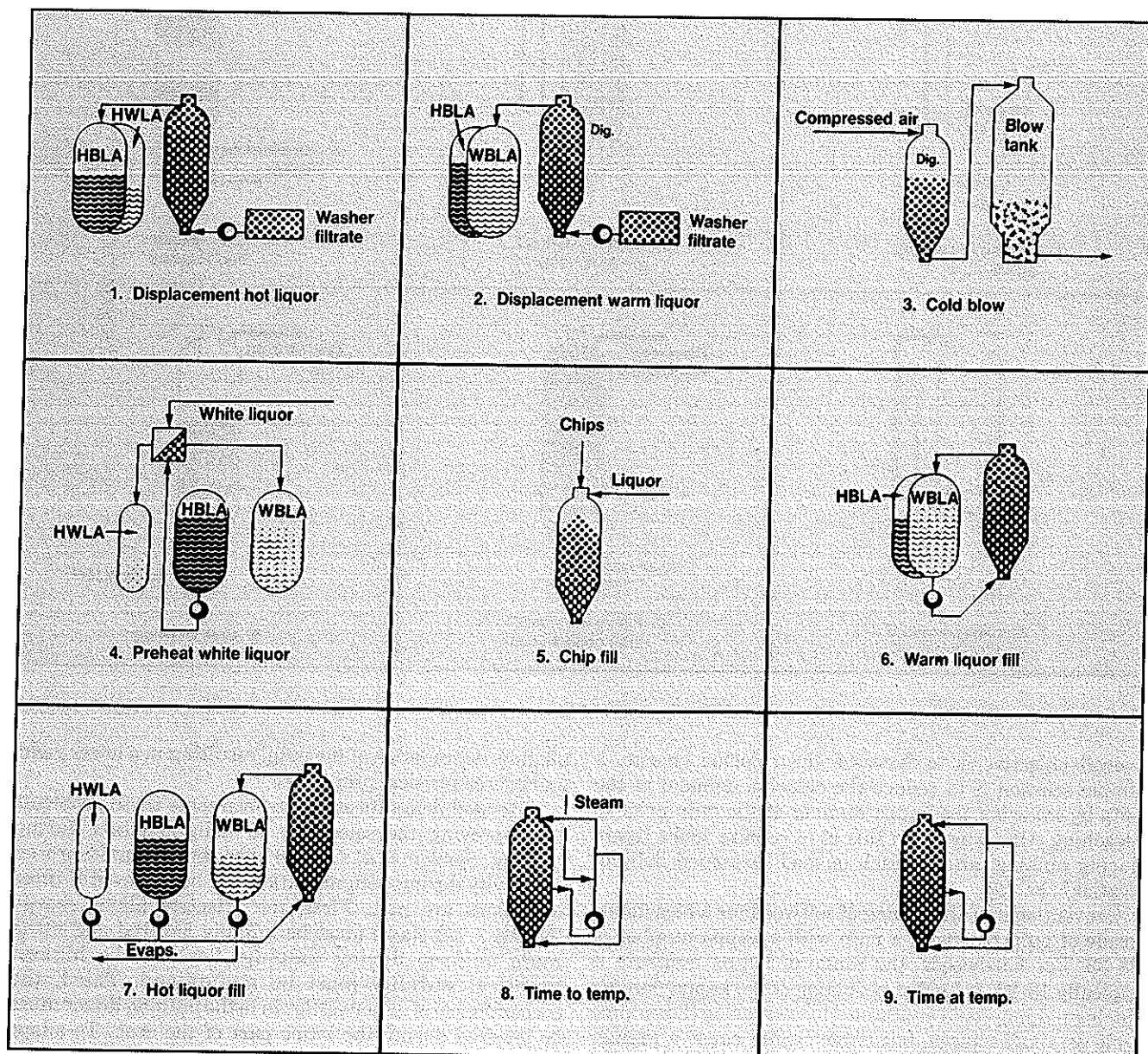
BOD<sub>7</sub> = biochemical oxygen demand.  
 COD = chemical oxygen demand.  
 TOC = total amount of organic carbon.  
 TOCl = Total amount of organically bound chlorine.

II. Characteristics of pulp and effluent, RDH extended delignification vs. conventional kraft pulping (24)

| Process                      | Kappa No. <sup>a</sup> | Total Active Cl <sub>2</sub> , % o.d. pulp | Brightness, % ISO | COD, kg/ton | BOD, kg/ton |
|------------------------------|------------------------|--------------------------------------------|-------------------|-------------|-------------|
| <b>Conventional kraft</b>    |                        |                                            |                   |             |             |
| Without O <sub>2</sub> stage | 34                     | 11.7                                       | 89                | 78          | 14          |
| With O <sub>2</sub> stage    | 23                     | 7.5                                        | 90                | 57          | 11          |
| <b>RDH extended</b>          |                        |                                            |                   |             |             |
| Without O <sub>2</sub> stage | 23                     | 9.0                                        | 88                | 50          | 10          |
| With O <sub>2</sub> stage    | 15                     | 5.3                                        | 88                | 40          | 8.5         |

<sup>a</sup>In pulp going to the bleach plant.

3. Operating cycle of the Beloit RDH system (HBLA = hot black liquor accumulator. HWLA = hot white liquor accumulator. WBLA = weak black liquor accumulator.)

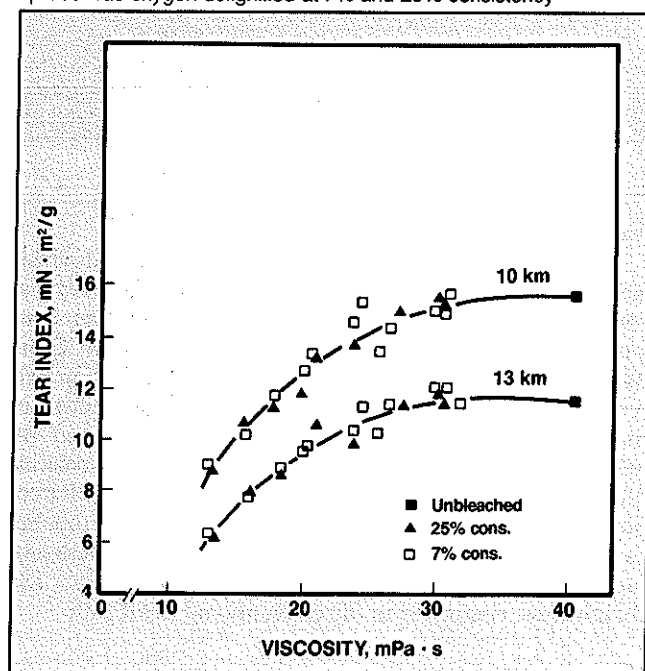


### III. Raw total mill effluent loads of alternative kraft pulping and bleaching processes (softwood)

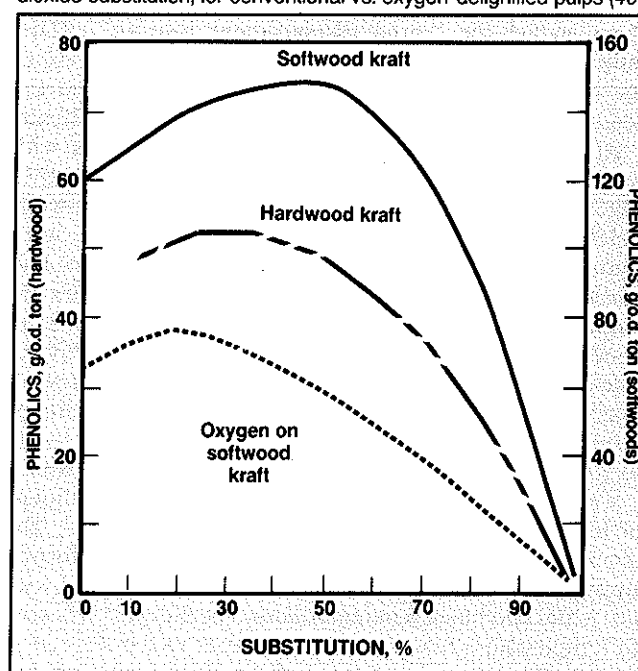
|                            | Unbleached<br>Kappa<br>no.* | BOD <sub>7</sub> ,<br>kg/a.d.<br>metric ton | COD,<br>kg/a.d.<br>metric ton | Color,<br>kg/a.d.<br>metric ton | TOC,<br>kg/a.d.<br>metric ton | Chlorinated<br>phenolics,<br>kg/a.d.<br>metric ton | Toxicity,<br>units/a.d.<br>metric ton |
|----------------------------|-----------------------------|---------------------------------------------|-------------------------------|---------------------------------|-------------------------------|----------------------------------------------------|---------------------------------------|
| (CD)(EO)DED                | 32                          | 25                                          | 115                           | 200                             | 5.5                           | 0.1                                                | 400                                   |
| After biological treatment |                             | 2.5                                         | 60                            | 200                             | 3.3                           | 0.08                                               | 60                                    |
| O(CD)(EO)DED               | 18                          | 20                                          | 80                            | 100                             | 3.5                           | 0.07                                               | 200                                   |
| After biological treatment |                             | 2.0                                         | 40                            | 100                             | 2.1                           | 0.06                                               | <50                                   |
| Modified cook              |                             |                                             |                               |                                 |                               |                                                    |                                       |
| O(CD)(EO)DED               | 25                          | 23                                          | 100                           | 160                             | 4.5                           | 0.08                                               | 350                                   |
| After biological treatment |                             | 2.3                                         | 50                            | 160                             | 2.7                           | 0.07                                               | 50                                    |
| Modified cook              |                             |                                             |                               |                                 |                               |                                                    |                                       |
| O(DC)(EO)D                 | 14                          | 19                                          | 70                            | 75                              | 2.5                           | 0.07                                               | 200                                   |
| After biological treatment |                             | 1.9                                         | 35                            | 75                              | 1.5                           | 0.06                                               | <50                                   |

\*Prior to the chlorination stage.

4. The effect of oxygen delignification on pulp quality (38), where black spruce was oxygen delignified at 7% and 25% consistency



5. Formation of total chlorinated phenolics with increasing chlorine dioxide substitution, for conventional vs. oxygen-delignified pulps (40)



these principles to the batch digestion of softwood, pulping is divided into two distinct periods between which the initial pulping liquor is displaced from the digester with a different liquor containing fresh pulping chemicals and a low lignin concentration. This approach meets the three conditions.

A mill trial of this concept was conducted at the ASSI mill in Karlsborg, Sweden (19). In the initial phase, the pulping liquor's effective alkali concentration was 15% on wood with sulfidity at 38%. The cook was conducted for 50 min to H-factor 1100 (vs. 60 min for the completion of a conventional cook). After the cook, the pulping liquor was displaced with another consisting of white liquor and washer filtrate and containing little lignin and 4% effective alkali at a sulfidity of 38%. The cook was continued for another 20 min, then relieved and blown. The kappa number of the resulting pulp was 25, as opposed to the

conventional pulp at 32, and pulp properties were unaffected. The pulp was bleached to 89% ISO brightness in a conventional (DC)EDED sequence using 20.1% less chlorine than was normally applied to the pulp at a kappa number of 32. The amount of TOCl produced in bleaching was reduced by 24.9%, compared to conventional bleaching.

#### Cold blow cooking

The main operational drawbacks to extended delignification are increased steam consumption and cooking time. These drawbacks have been overcome by coupling this technology with a system developed by Sunds Defibrator called "cold blow cooking" (19, 20).

The cold blow cooking system (Fig. 2) employs a displacement of the spent cooking liquor with washer filtrate prior to blowing the pulp from the digester at a

temperature below 100°C. The displaced black liquor is sent to a strong liquor pressure accumulator. The heat from this liquor is recovered to pre-heat the white liquor. Subsequent digester charges are made using the pre-heated white liquor and hot black liquor from the liquor accumulator. Consequently, heating the digester to its cooking temperature will require less time and will consume 40–50% less steam.

A mill trial of this combination of extended delignification and cold blow cooking (21) demonstrated that a reduction to a kappa number of 25 from a range of 30–32 could be accomplished, along with a 30–35% decrease in steam consumption. Effluent parameters were monitored (Table I), and a 24.9% reduction in TOCl was achieved. Pulp quality and viscosity were maintained. In addition, pulp produced via the cold blow technique was easier to wash because its drainability had been improved.

### Rapid displacement heating

Concurrent with these developments, another extended delignification process has been developed by the Beloit Corp. called the “rapid displacement heating” (RDH) pulping system (22, 23). The RDH system (Fig. 3) involves the recovery of digester heat via displacement and the accumulation of the hot black liquor with washer filtrate.

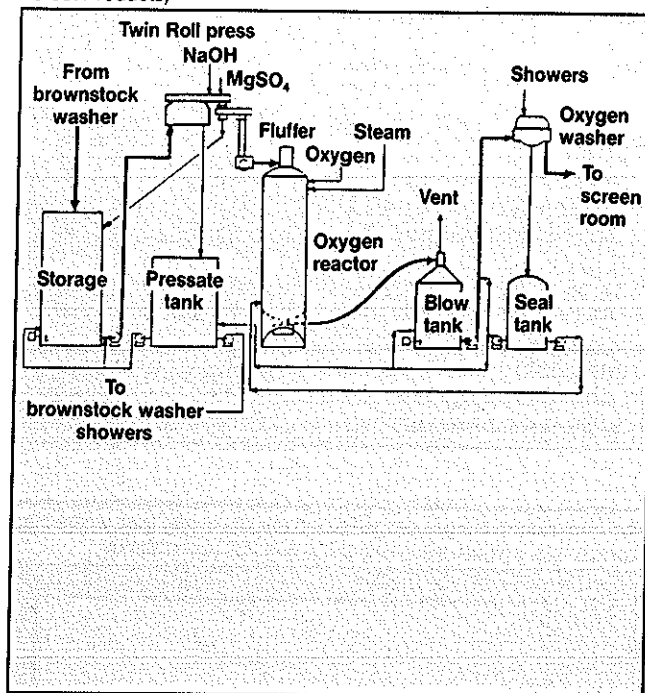
At the end of the cook, displacement continues with washer filtrate until the pulp temperature is about 80°C. The displaced liquor at this point is collected in a weak black liquor accumulator. The pulp is blown with compressed air rather than steam, for a faster blow and additional savings in steam. Special heat exchangers are employed to pre-heat the white liquor (which is stored in another accumulator) for the next cook to about 155°C. The digester is charged with chips and packed with weak black liquor, which is introduced through special liquor nozzles. This technique increases packing density by up to 10%, thereby increasing pulp production per digester.

The digester is hydraulically filled with warm liquor of high-sulfidity (low active alkali) at about 100°C. The elevated pressure in the digester serves to uniformly impregnate the chips. The warm liquor is displaced with hot white and black cooking liquors. The digester is heated to temperature, and the cook continues to the desired H factor. Displacement of the cooking liquor with washer filtrate terminates the cook.

Results using the RDH system (24) indicate that a kappa number reduction from 33.5 to 18.9 on softwood is possible, with an accompanying reduction in the chlorine required for bleaching. The pulp made via extended delignification was bleached to 90% ISO brightness using 7.5% active chlorine vs. 11.7% active chlorine (number includes the  $\text{ClO}_2$  charge) to bleach the conventional kraft pulp to an equivalent brightness. Further pertinent data is included in Table II. Caustic soda consumption also decreased from 4.3% to 2.7%. Pulp strength properties were equal to or superior to the conventional kraft pulp.

The RDH pulping system has been demonstrated commercially (23, 25, 26). At the Joutseno Oy mill in Finland, the kappa number was reduced from a range of 30–32 down to 21–22, with an accompanying increase in strength properties. Chlorine consumption was reduced by 25%. Steam consumption was decreased 60–65%. White liquor consumption was decreased, and poor quality chips

6. Typical oxygen delignification system (43) (Courtesy of E.B. Eddy Forest Products)



were easily pulped.

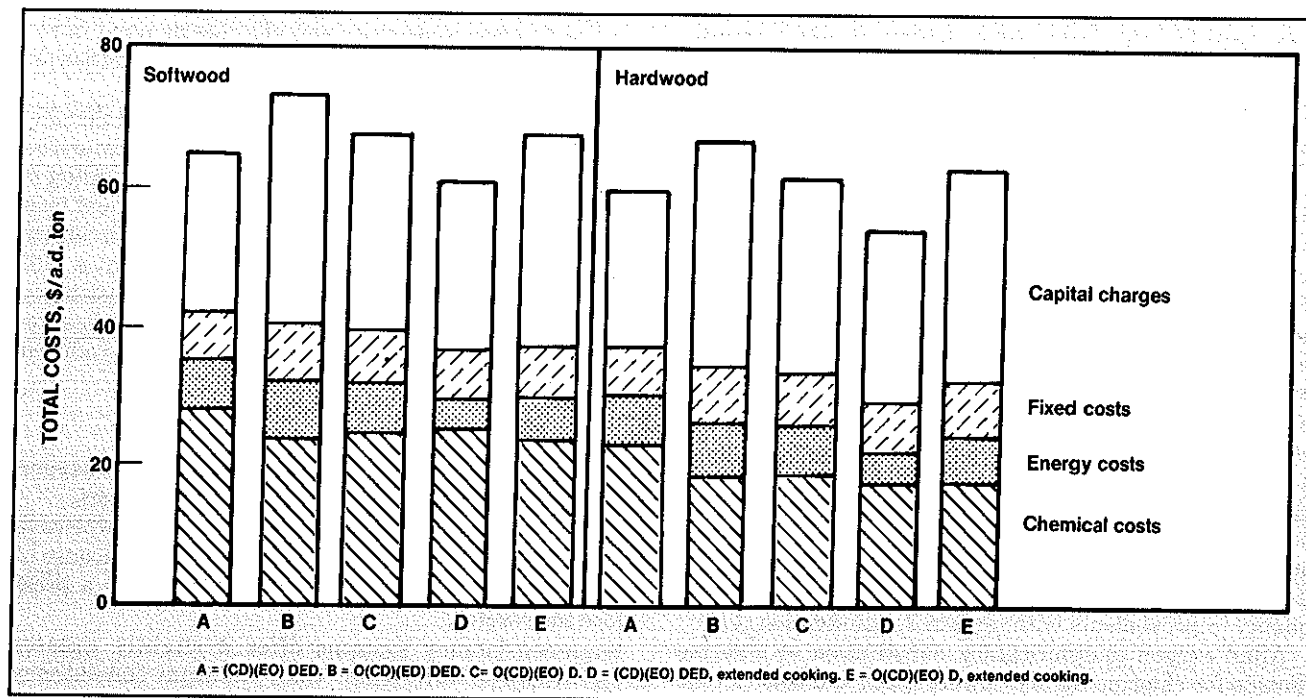
The principles of extended delignification have also been adapted to continuous pulping. The process is known as “modified continuous cooking” (MCC) and has been operated on a commercial scale since 1983 (27). MCC has been accomplished through the modification of a two-vessel Kamyr continuous digester to allow both the introduction of white liquor at several points and the countercurrent flow of the liquor during the final cooking phase. Kappa number reductions of 8 units for softwood and 4–5 units for hardwood have been accomplished without loss of strength properties. About 20–25% less total active chlorine is needed to bleach the pulp to 88% ISO brightness, compared to the conventional kraft pulp.

### Oxygen delignification

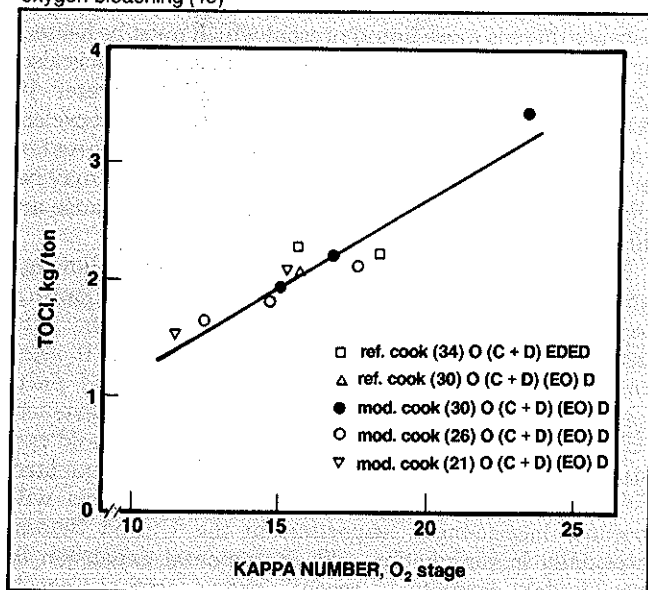
Another method that has been successfully employed to delignify pulp prior to bleaching is oxygen delignification. It was developed as a commercially feasible process for the bleaching of chemical pulps during the late 1960s and early 1970s. Although laboratory experimentation was done prior to this, it was the discovery that magnesium compounds protect pulp strength which enabled oxygen delignification to become practical in the mill (28). In 1970, the SAPPI mill in South Africa started up the first oxygen delignification stage in the world. Today, there are 47 oxygen delignification stages operating, producing a total of 8.3 million metric tons per year of pulp worldwide (29).

Oxygen delignification can now be done in either medium- or high-consistency systems. The choice of deciding which to install is often specific to economics and technical needs at a particular site. Oxygen delignification is used for various reasons; in Japan to lower bleaching costs, in Scandinavia to lower effluent toxicity, and in

7. Estimated total bleaching costs (Swedish softwood and hardwood) (40)



8. TOCl in combined spent bleaching liquors vs. kappa number after oxygen bleaching (49)



North America to assist in the economics of bleach plant modernization or expansion (30-32). However, an oxygen delignification stage is increasingly being proposed as a favorable method of reducing active chlorine demand during bleaching, thereby decreasing the quantity of chlorine-containing compounds in aqueous effluent and gaseous emissions from a bleach plant.

Hydrogen peroxide has also been discussed as a source of oxygen during prechlorination delignification and has been used as such at several commercial locations (33). However, its use as the sole oxidizing agent in this sense

is generally not justified economically. Various pretreatment methods have been proposed prior to delignification with oxygen that are designed to improve the selectivity of oxygen for lignin. The best results were obtained when done under acidic pH conditions and when including combinations of nitrogen dioxide and oxygen (Prenox.) (34) or hydrogen peroxide and oxygen (35).

#### The effect on pulp quality

The strength properties of oxygen-delignified pulp are not harmed as long as the degree of delignification does not exceed about 50% (36). A mill survey by the TAPPI Oxygen Delignification Committee reported in 1984 that for bleached, market-grade kraft pulp, oxygen delignification results in 5-15% lower viscosity, 0-10% lower burst, 0-10% lower tensile strength, and the same tear strength properties (37). The survey also indicated that various factors can have a detrimental effect on pulp viscosity and strength including transition metals, excess alkali charge, black liquor carryover, and low reaction pressure.

Liebergott (38) showed in recent laboratory work that consistency of oxygen delignification over the range of 7-25% resulted in similar pulp strength properties. The black spruce pulp used in these experiments exhibited a tear deficiency if viscosity fell below 20 mPa. The relationship between tear and constant breaking length is shown in Fig. 4. It is quite important to select parameters during delignification which will yield the least viscosity loss at the kappa number target. These parameters include temperature, alkali charge, retention time, and oxygen pressure.

Oxygen delignification has been reported in a number of commercial applications to be effective in dirt and bark removal (39). When sulfite pulp is delignified with oxygen, there is also a beneficial effect in pitch removal, and the

lowering of extractives content of fully bleached pulp has been seen in kraft mills. These benefits probably result from pressing the pulp either before or after oxygen treatment.

#### Effect on effluent quality

The effluent load of a bleach plant preceded by an oxygen delignification stage is reduced for several important reasons. First, filtrate leaving post-oxygen washers is usually recycled back to the kraft recovery furnace, where it is burned. Second, the degree of pulp delignification by oxygen directly affects the chemical charge that must follow for further delignification and bleaching. Third, the benefits of oxygen delignification are also additive to those achieved from reduction in kappa number by extended cooking. Table III illustrates effluent load parameters for softwood pulp bleached by several different sequences to a 90% ISO brightness, both before and after secondary biological treatment (40). In the United States, most mills have secondary biological treatment, whereas in Canada and Europe, this is not always the case. Fully bleached hardwood kraft mills have demonstrated similar effluent quality improvements with oxygen delignification (41).

After oxygen delignification, substitution of chlorine dioxide for chlorine further lowers TOCl and color levels. High percentages of substitution of 50% or more decrease the formation of chlorinated phenolics. However, in the substitution of chlorine dioxide for chlorine, the total amount of chlorinated phenolics formed increases as substitution increases. A maximum is reached at about 50% substitution for conventionally bleached pulp.

Liebergott has characterized the chlorinated phenolics in effluent from the first two stages (CD)(EO) or (DC)(EO), comparing percentages both with and without a preceding oxygen pretreatment (42). His findings are as shown in Fig. 5 (40). Other recently published data have suggested that a practical approach to reaching low TOCl targets for certain Swedish mills is to practice oxygen delignification followed by high substitution of chlorine dioxide for chlorine (31).

#### Commercial implementation

There are two commercially accepted oxygen delignification processes: medium consistency (8–17%) and high consistency (22–28%). Both are being installed today, but there is a definite trend toward medium consistency because of lower capital costs, even with the penalty of slightly lower delignification capabilities (45% vs. 50%). A typical oxygen delignification stage is illustrated in Fig. 6 (43).

Two high-consistency systems are available: the Sapoxal™ process and the MoDo-CIL™ process. The major difference in these systems is in the design of the reactor vessel. Discussions of these systems can be found in other publications (43, 44).

Medium-consistency oxygen delignification became feasible when it was discovered that oxygen can be mixed into medium-consistency pulp in a turbulent state as small bubbles and that the stock will prevent the recombination of the bubbles. At a lower limit of about 8% consistency, the oxygen rises in channels through the pulp up the bleaching reactor. Two-stage washing is usually carried out before the reactor, and two washing stages are common

after the reactor, usually followed by a press. Post-oxygen washing efficiency is important because it contributes to chemical recovery economics and chlorine demand in the next stage and because it minimizes the formation of chlorinated organics.

Recent laboratory and pilot studies have shown that 25–30% delignification can be achieved in a nonpressurized medium-consistency oxygen stage (45, 46). This finding is further incentive for reducing the effluent treatment load at a much lower capital investment cost than either medium- or high-consistency systems. Eventually, a mill may be able to retrofit an existing medium-consistency tower and practice nonpressurized oxygen delignification in an (EO)(CD)(EO)D bleach sequence, with reduced chlorine requirements.

#### Investment economics

The relative economics of a decision to invest in an oxygen delignification system depend on several key factors.

High-consistency systems are normally more expensive to purchase than medium-consistency systems because of more complex reactor controls and the need for a press before the reactor.

High-consistency systems offer a slightly greater delignification efficiency than medium-consistency systems. Thus, medium-consistency oxygen delignification leaves more lignin to be removed in the bleach plant, resulting in a higher chlorine demand and the formation of more chlorinated organics.

Medium-consistency systems require more steam input because there is more liquid present which must be heated to the reaction temperature. A higher alkali charge is also necessary to compensate for additional dilution water. If vent gases from a high-consistency system are not recycled back to the reactor, oxygen requirements can be greater in a high-consistency system. Power requirements may be slightly greater in a high-consistency system because an additional press is needed before the reactor.

Depending on the type of bleaching sequence following an oxygen bleaching stage, the overall costs of adopting oxygen delignification into a mill will vary. Also, the costs depend on chemical costs at the specific mill site. Integrated kraft mills with a target bleached pulp brightness of 85–87% ISO can bleach with a shortened (CD)(EO)D sequence following oxygen bleaching and can still achieve operating economics favorable to a standard five-stage (CD)(EO)DED sequence. This scenario will become increasingly important in the United States, especially in conjunction with incremental expansion in bleach plant capacity, as recently experienced at Consolidated Paper's Wisconsin Rapids mill (32).

Market kraft mills requiring 89–90% ISO final brightness have a difficult time achieving required brightnesses with a shortened bleach sequence. Thus, five-stage bleaching may still be required. Alternatively, hydrogen peroxide may be used either as a reinforcing chemical in an (EO) stage or as a final bleaching treatment. Figure 7 illustrates total bleaching costs for various bleaching alternatives (40). In this example, oxygen delignification is done at medium consistency, and the brightness targets for hardwood and softwoods are 89% ISO and 90% ISO, respectively. The conclusion is that oxygen delignification followed by a short bleaching sequence is competitive in

costs to a standard sequence but is more expensive to operate when followed by a five-stage bleach sequence.

### Pretreatment processes

Various pretreatment steps have been developed to improve the selectivity of oxygen for lignin during delignification. Some have progressed beyond the laboratory and into pilot plant and commercial units in the mill. The most work has been done by Samuelson and others in Sweden using nitrogen dioxide and oxygen in an acidic medium (34). This process has been patented and is referred to as the Prenox process. The Prenox-O<sub>2</sub> bleaching combination offers the possibility of lowering the kappa number by 3-6 units without severe strength losses in the pulp. Improvements in the Prenox process offer much hope for its future use in commercial mills that desire to have low bleach plant effluent loads (47).

Hydrogen peroxide is another chemical which may prove useful during acidic pretreatment processes to improve the efficiency of oxygen delignification. A patented process by Mo och Domsjo suggests using H<sub>2</sub>O<sub>2</sub> at a pH of 0.5-4.0 to pretreat pulp, resulting in lower demand for chlorine in the bleaching sequence (48). More recent work has involved the use of hydrogen peroxide and oxygen as an acidic pretreatment to an ordinary oxygen delignification stage (35). The potential exists for a 5-10% lower kappa number after oxygen delignification. However, the process appears to give better results on sulfite than kraft pulp, requiring improvements in sulfite pulping before commercialization is expected.

### Combination of oxygen and extended delignification

The gains in delignification that can be achieved via extended delignification in the digester are additional to oxygen delignification. The combination of these two technologies (45) results in reductions in TOCl formation (Fig. 8). The combination of simulated modified continuous cooking of pine chips and oxygen delignification reduced the kappa number of the pulp to 11. The pulp was bleached to 90% ISO brightness in a (C+D)(EO)D sequence. TOCl in the combined spent bleaching liquors was reduced to about 1.5 kg/metric ton vs. about 3.4 kg/metric ton for the reference pulp, which was bleached in an O(C+D)(EO)D sequence.

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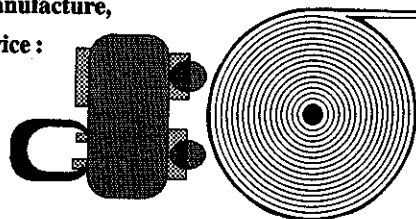
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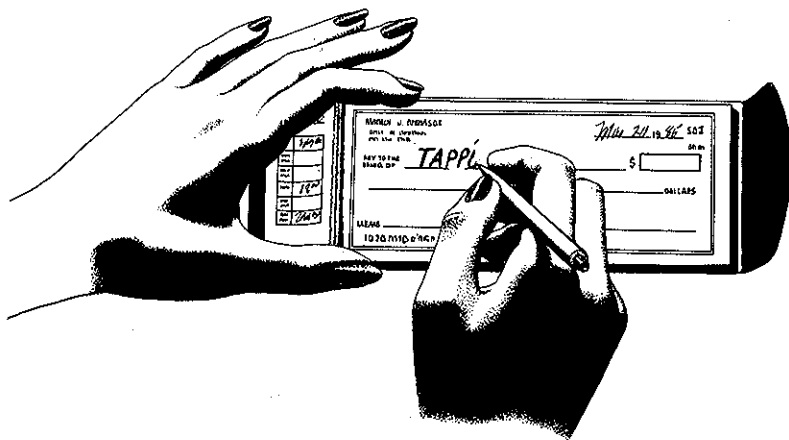
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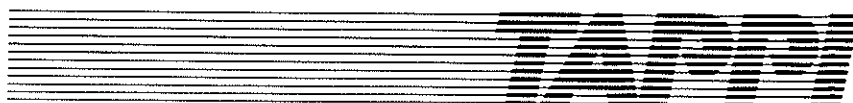
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