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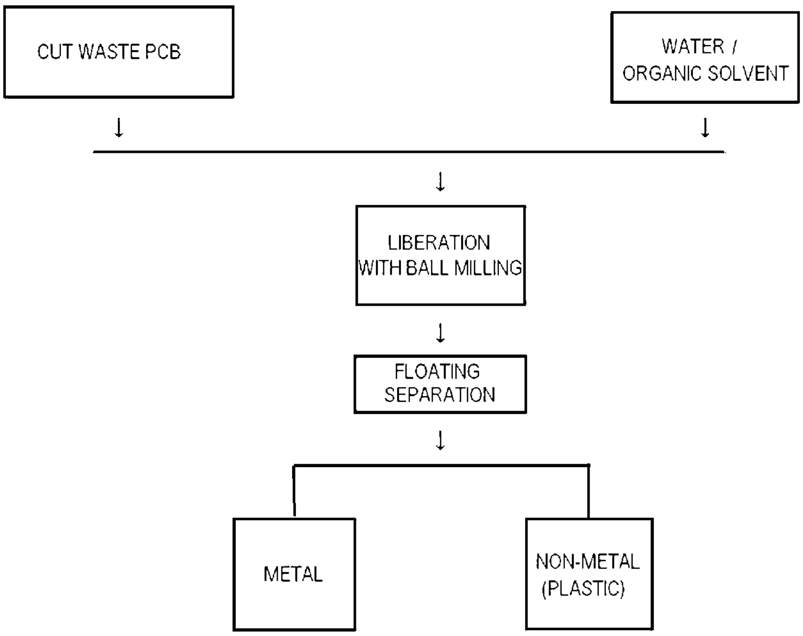
(54) Title: METHOD FOR RECOVERY OF METALS FROM WASTE PRINTED CIRCUIT BOARDS



(57) Abstract: Provided is a method for recovery of metals from waste PCBs including (a) injecting water into cut waste PCBs and conducting ball milling to liberate metals and plastics from each other to thereby prepare a mixture containing the metals, the plastics and water; and (b) using the mixture as a pulp solution and subjecting the pulp solution to floating separation to separate and recover the liberated metals. The present invention provides increased separation efficiencies of metal components and non-metal components from the waste PCBs, and particularly, provides a simple and economic process that can recover the metal components existing in the plastic components.

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Description

Title of Invention: METHOD FOR RECOVERY OF METALS FROM WASTE PRINTED CIRCUIT BOARDS

Technical Field

[1] The present invention relates to a method for recovery of valuable metals contained in waste printed circuit boards.

[2]

Background Art

[3] In general, waste printed circuit boards (waste PCBs) contain large amounts of valuable metals such as iron, copper, aluminum and nickel along with noble metals such as gold, palladium and silver.

[4] Recently, rapid changes in shape and performance in electronic devices in order to meet customer needs have led to short life cycles of the electronic devices, which has induced an increase in an amount of the waste PCBs generated. Thus, disposal of electronic wastes (e-wastes) is becoming a heavy burden for the manufacturers, and environmental contamination from the e-wastes is also becoming a social problem. On the other hand, the waste PCBs contain plenty of valuable metals that can be recycled by a proper treatment, and thus recycling of the valuable metals is very useful in terms of resource utilization of the waste PCBs and reducing environmental contamination.

[5] In order to recover valuable metals from the waste PCBs, non-metal components which constitute approximately 40 to 70% of the waste PCBs should be removed. Processes for separating the metal components and plastic components from the waste PCBs are largely classified as physical separation processes and wet processes.

[6] In the prior art, Korean Laid-open Patent Publication No. 2003-0006792 (Patent Document 1) discloses a process of recovering valuable metals from waste PCBs including subjecting the waste PCBs to crushing, air separation, electrostatic separation or magnetic separation, dissolving/separating copper, iron, zinc, nickel and aluminum components with sulfuric acid and hydrogen peroxide, dissolving/separating gold and silver with aqueous $(NH_4)_2S_2O_3$, $CuSO_4$ and NH_4OH solutions, dissolving/separating lead with saline, and dissolving/separating palladium with aqua regia.

[7] Korean Laid-open Patent Publication No. 2001-0067641 (Patent Document 2) discloses a process of recovering noble metals from waste PCBs using chelate resins including subjecting the waste PCBs to crushing, dissolving metal components to adsorb onto chelate resins, and desorbing noble metals adsorbed on the chelate resins with an eluent to recover the noble metals.

[8] Korean Laid-open Patent Publication No. 2007-0077114 (Patent Document 3)

discloses a process including recovering tin using high temperature melting and a tin scavenging solution, dissolving/separating copper using a strong acid solution, separating a brominated epoxy resin from a fiber glass via a thermo-chemical reaction using sodium nitrate, and separating/recovering a carbonized fiber glass and copper flakes using water washing.

[9] When using wet processes as disclosed in Korean Laid-open Patent Publication Nos. 2003-0006792 and 2001-0067641, although metal components are recovered through leaching of metals from the waste PCBs using acids, criteria that determine leaching rates are not provided therein, and, therefore, they cannot help but depend on the past experiences. Further, one of the disadvantages that they have is that excessive wastewater is generated, which still has made commercialization difficult.

[10] In contrast, when using physical separation process as disclosed in Japanese Laid-open Patent Publication No. 2005-324176 (Patent Document 4), although it could be advantageous that it is simple and wastewater is not generated, its separation efficiencies in separating metal components and non-metal components from waste PCBs using such process were found to be low. Further, it is known that it is not possible to recover the metal components present in between the plastic components, and thus increased loss of the metal components may occur.

[11]

Disclosure of Invention

Technical Problem

[12] An object of the present invention is to provide a simple and economical method for recovery of metals from waste printed circuit boards that is capable of increasing separation efficiency of metal components and non-metal components, does not generate wastewater, and particularly, is capable of recovering metal components existing in plastic components.

[13]

Solution to Problem

[14] In one general aspect, a method for recovery of metals from waste PCBs includes: (a) injecting water into cut waste PCBs and conducting ball milling to liberate metals and plastics from each other to thereby prepare a mixture containing the metals, the plastics and water; and (b) using the mixture as a pulp solution, and subjecting the pulp solution to floating separation to separate and recover the liberated metals.

[15] The cut waste PCB may have a particle size of 20 mm to 30 mm.

[16] The cut waste PCB may be introduced in the amount of 70 to 120 g per 1 L of water.

[17] The ball milling may be conducted by stirring at a temperature of 90 to 140℃.

[18] The ball milling may be conducted at a revolution rate of 400 to 600 rpm for 30 to

120 minutes.

[19] The balls used for the ball milling may be metallic balls or ceramic balls having a particle size of 10 to 15 mm.

[20] An amount of the injected balls may be in the range of 5 to 10% of a volume of a grinding machine in the ball mill.

[21] In the floating separation, 0.001 to 2% by weight of a floatation reagent may be added to the pulp solution to float and recover the liberated metals.

Advantageous Effects of Invention

[22] The method for recovery of the metals from the waste PCBs according to the present invention can separate and recover metal components from non-metal components, such as plastic components, particularly, the metal components existing in the plastic components by splitting multiple layers of laminated plastics through the liberation of metal components and plastic components using ball milling. Moreover, the present method is simple since it recovers the metals through floating separation without any separate drying and sieving processes after the liberation, and further the present method can obtain at least 99.9% of metal recovery rate.

[23]

Brief Description of Drawings

[24] FIG. 1 illustrates a method for recovery of metals from waste PCBs according to the present invention.

[25]

Best Mode for Carrying out the Invention

[26] The above and other objects, features and advantages of the present invention will become apparent from the following description on preferred embodiments given in conjunction with the accompanying drawing. Hereinafter, the present invention will be described in detail with reference to the accompanying drawing, in which the drawing is presented for illustration purpose only to make a person of ordinary skill in the art best understand the present invention. Therefore, it is intended that the present invention is not limited to the drawing described herein, but various other forms equivalent thereto may be contemplated.

[27] The present method provides a method for recovery of metals from waste PCBs including (a) injecting water into cut waste PCBs and conducting ball milling to liberate metals and plastics from each other to thereby prepare a mixture containing the metals, the plastics and water; and (b) using the mixture as a pulp solution and subjecting the pulp solution to floating separation to separate and recover the liberated metals.

[28] Hereinafter, the present invention will be described in more detail with reference to

the accompanying drawing.

[29] First, in step (a), water is injected into cut waste PCBs and ball milling is conducted to liberate metals and plastics from the waste PCBs to thereby prepare a mixture containing the metals, the plastics and water.

[30] FIG. 1 shows an example that illustrates a method for recovery of the metals from the waste PCBs according to the present invention.

[31] As illustrated in FIG. 1, water is poured onto the waste PCBs and ball milling is conducted to liberate metals and plastics from the waste PCBs.

[32] The waste PCBs may be cut using cutting machines commonly used in the art, and preferably cut to a particle size of 20 mm to 30 mm.

[33] The metal components may be metal plates attached to plastic plates with organic adhesives, and include metal layers, thin metal flakes or metallic bodies which are present on the plastic plates using thermal or mechanical pressure such as electro-chemical plating, vapor deposition, soldering or rolling.

[34] The non-metal components may include plastic plates or glass fiber plates.

[35] When the plastic plates and the metal components are bonded with or without organic adhesives, the plastic plates are separated by physical forces caused by the balls contained in the ball milling, and consequently the liberation of the plastic plates and the metal components occurs.

[36] Any ball milling for the liberation may be used herein. A ball milling for the liberation process is mainly classified on four major principles; compression, impact, rubbing and cutting. A grinding mechanism is known to have large effects on grinding efficiency as well as characteristics of grinded products, such as grain-size distribution and generation of fine powder.

[37] In order to readily perform the liberation process in the present invention, the principle of the impact should be applied during the liberation process. We have found that, in order to recover metal components existing in plastic components, among other things, ball milling may be employed in the present invention, and as a result the separation rate of metals and plastics surprisingly increased by at least 99.9%, and at last has completed this invention accordingly.

[38] Preferably, in order to effectively perform the liberation with the ball milling, the waste PCBs may be cut to a particle size of up to 30 mm, prior to liberation. Although the smaller the cut size is, the shorter the time spent in liberating the metals and plastics becomes, the disadvantage is that the time spent in the cutting process is too long, and when the cut size is greater than 30 mm, the liberation of the metals and plastics with a grinding machine may not be readily performed. As such, more preferably, the cut waste PCBs have a particle size of 20 to 30 mm.

[39] Preferably, in order to effectively perform the liberation, the waste PCBs may be in-

troduced in the amount of 70 to 120 g per l L of water. When less than 70 g of the waste PCBs are made per water, the separation efficiency for the period of the same stirring time is minute. When greater than 120 g of the waste PCBs are made per water, effective stirring may not be achieved, and as a result the separation efficiency may be decreased.

[40] The water may be used as a solvent during the liberation of the metals and plastics. When using the water, liberation rates of the metals and plastics may be increased without other side reactions with organics, and the floating separation may proceed using the pulp solution as a solvent where the metals and plastics are liberated therefrom. This surprisingly efficient process is a simple and an environment-friendly process for the recovery of the metals.

[41] Although the water may be used as a solvent for the liberation of the metals and plastics, organic solvents may be additionally used to dissolve organic adhesives where applicable. When the organic solvents are added, the liberation of the metals and plastics may be facilitated due to the dissolution of the organic adhesives. When the plastic plates and the metal components are bonded without the organic adhesives, the organic solvent may be permeated through the interface formed between the plastic plates and the metal components so that the organics in the interface may be dissolved to facilitate the liberation of the metals and plastics.

[42] The organic solvents include N,N-dimethyformamide ($HCON(CH_3)_2$), methyl ethyl ketone ($CH_3COC_2H_5$), tetrahydrofuran (C_4H_8O), Stripoxy or the combinations thereof, preferably N,N-dimethylformamide. The content of such organic solvents are not limited, but approximately 0.1 to 10% by weight may be preferably used.

[43] In order to perform the liberation of the metals and plastics more effectively, it is preferred that the stirring may be conducted at a revolution rate of 400 to 600 rpm at a temperature of 90 to 140℃.

[44] It is possible to enhance the activity of the water or the organic solvent and to minimize the loss of the organic solvent due to its volatilization by conducting the stirring at a temperature of 90 to 140℃.

[45] Further, the stirring may be conducted at a revolution rate of 400 to 600 rpm, wherein a rod in which a transverse pin is installed capable of stirring metals or ceramic balls may be used. The revolution at 400 to 600 rpm is a stirring condition optimized to enhance the separation efficiency by applying physical impact to the cut waste PCBs and to transfer to a substrate the physical forces generated from the rotations of the balls.

[46] The stirring at the above revolution rate of 400 to 600 rpm is preferably conducted for about 30 minutes to about 2 hours. When less than about 30 minutes, the liberation of the metals and plastics may not be achieved, and when greater than about 2 hours,

the increase of the separation efficiency is not effective.

[47] The balls used for the ball milling are not limited, but metallic balls or ceramic balls are preferred.

[48] The size of the balls used for the ball milling is not limited, but a particle size of 10 to 15 mm is preferred. When a particle size thereof is less than 10 mm, loads applied to the motor while stirring are too high, so the stirring is not conducted smoothly, and when a particle size thereof is greater than 15 mm, the liberation efficiency is decreased.

[49] An amount of the injected balls may be in the range of 5 to 10% of a volume of a grinding machine in the ball mill. When the injected amount is less than 5%, the liberation efficiency is decreased, and when the injected amount is greater than 10%, loads applied to the motor while stirring is too high, so the stirring is not conducted smoothly.

[50] By way of conducting the ball milling, the separation rate of the metals and the plastics may reach at least 99.9%.

[51] Next, in step (b), the mixture may be used as a pulp solution, and the pulp solution may be subjected to floating separation to separate and recover the liberated metals.

[52] Since the liberated mixture may be directly used as a pulp solution for floating separation, any separate processes, such as sieving, drying, washing, etc., may be reduced, and the potential losses in sieving and washing processes during the recovery of the metals may be excluded, and as well as more an efficient separation is possible by increasing recovery rate.

[53] Further, since the liberated mixture may be directly used as a pulp solution without any separate washing process and thereby wastewater may not be generated, step (b) is an environment-friendly process.

[54] This is not found in the prior art, and is a remarkably unexpected process since it can solve the problem that has been encountered by the prior art that, when the liberation and floating separation steps are consecutively practiced, the intermediate processes, such as sieving, washing, drying, etc., are to be used, and thereby the efficiencies become decreased. Further, since this process does not generate wastewater, so it is environment-friendly. Accordingly, the present invention can also satisfy both of the recovery rate requirements of the metals, and the economic and environment-friendly issues.

[55] In particular, as depicted in FIG. 1., in step (b), the mixture containing the metals, the plastics and water may be directly used as a pulp solution, and the pulp solution is subjected to floating separation to separate and recover the liberated metals.

[56] In such case, the floating separation may be optionally employed whenever necessary. A floatation reagent may be added to the pulp solution in the range of 0.001

to 2% by weight to make the liberated metals float and be recovered. When the content of the floatation reagent is less than 0.001% by weight, it is not effective, and when it is greater than 2% by weight, the efficiency of the floatation reagent based on the injected amount is problematic. The floatation reagent plays a role in reducing time spent in floating separation.

[57] The floatation reagent includes a foaming agent commonly used in the art. The floatation reagent may be added in the range of 0.001 to 2% by weight to the pulp solution so that it mechanically or chemically facilitates the formation of air bubbles to help the liberated metals to float and be separated.

[58] An exemplary foaming agent may include a surfactant that commonly serves as a foaming agent. The foaming agent finely disperses a large amount of air introduced by a mechanical stirrer and forms foam layers on the surface of the pulp solution. For example, pine oil, methyl isobutyl carbinol (MIBC), polypropylene ether, polyglycols, cresylic acid, triethoxy butane (TEB), Cyanamid AF65 or DowFroth 250 may be used herein.

[59] Meanwhile, collector or conditioning agents are not used since the effect of the addition of such agents is not significant.

[60] The floating separation indicates the floatation caused by the floatation reagent. The floatation includes hydrophobicizing and stirring the plastics in the liberated mixture of the metals and the plastics, and then attaching the plastics to bubbles to separate them, thereby allowing the separation and the recovery of high quality metals.

[61] The present invention, if necessary, may further include separating the metals and the plastics with the water through conventional sieving, after performing the liberation with the ball milling prior to the floating separation. Further, the water recovered through the sieving may be reused as the water to be injected into the cut waste PCBs, as depicted in FIG. 1.

[62] Further, the metal components and the plastic components recovered through the sieving may also go through washing and drying, and then the metal components may be separated and recovered from the non-metal components (e.g., plastics).

[63] Example 1

[64] The waste PCBs were cut with a mean particle size of 30 mm and introduced into a beaker in the amount of 100 g per 1 L of water. The temperature was maintained at 90°C, and 50 ceramic balls with a diameter of 1 cm (which occupies 5% by a volume of grinding machine) were put into the grinding machine, then stirred at the revolution rate of 600 rpm for 1 hour using a bar 20 cm long with 4 pins having the transverse length of 4 cm. After completing the stirring, the liberated mixture was used as a pulp solution and stirred for one and a half minutes, then water and air were introduced thereinto, followed by performing the floating separation (Metso model: L3409-50,

1000rpm) in water for three and a half minutes without adding additional reagents, thereby obtaining 99.9% of metal recovery rate.

[65] Example 2

[66] This Example was prepared and tested in analogous to Example 1 except that the waste PCBs were cut with a mean particle size of 25 mm.

[67] Example 3

[68] This Example was prepared and tested in analogous to Example 1 except that the waste PCBs were cut with a mean particle size of 20 mm.

[69] Table 1 below summarizes the metal recovery rates for each size of the cut waste PCBs.

[70]

[71] Table 1

[Table 1]

	Test result of floating separation		
	Cut size	Liberation rate	Metal recovery rate
Example 1	30 mm	99.0%	99.9%
Example 2	25 mm	99.9%	99.9%
Example 3	20 mm	99.9%	99.9%

[72] As can be seen from Table 1 above, the method for recovery of metals from the waste PCBs according to the present invention shows 99.9% of liberation rates and 99.9% of metal recovery rates. However, the present invention is not limited to the embodiments described above, and various changes and modifications to the preferred embodiments from the foregoing descriptions may be made by a person of ordinary skill in the art without departing from the spirit and scope of this invention.

[73] Therefore, the sprit of the present invention should not be limited to the above-described exemplary embodiments, and the following claims as well as all modified equally or equivalently to the claims are intended to fall within the scopes and spirits of the invention.

Claims

[Claim 1] A method for recovery of metals from waste printed circuit boards (waste PCBs), the method comprising:

(a) injecting water into cut waste PCBs and conducting ball milling to liberate metals and plastics from each other to thereby prepare a mixture containing the metals, the plastics and water; and

(b) using the mixture as a pulp solution and subjecting the pulp solution to floating separation to separate and recover the liberated metals.

[Claim 2] The method of claim 1, wherein the cut waste PCB has a particle size of 20 mm to 30 mm.

[Claim 3] The method of claim 1, wherein the cut waste PCB is introduced in the amount of 70 to 120 g per 1 L of water.

[Claim 4] The method of claim 1, wherein the ball milling is conducted by stirring at a temperature of 90 to 140℃.

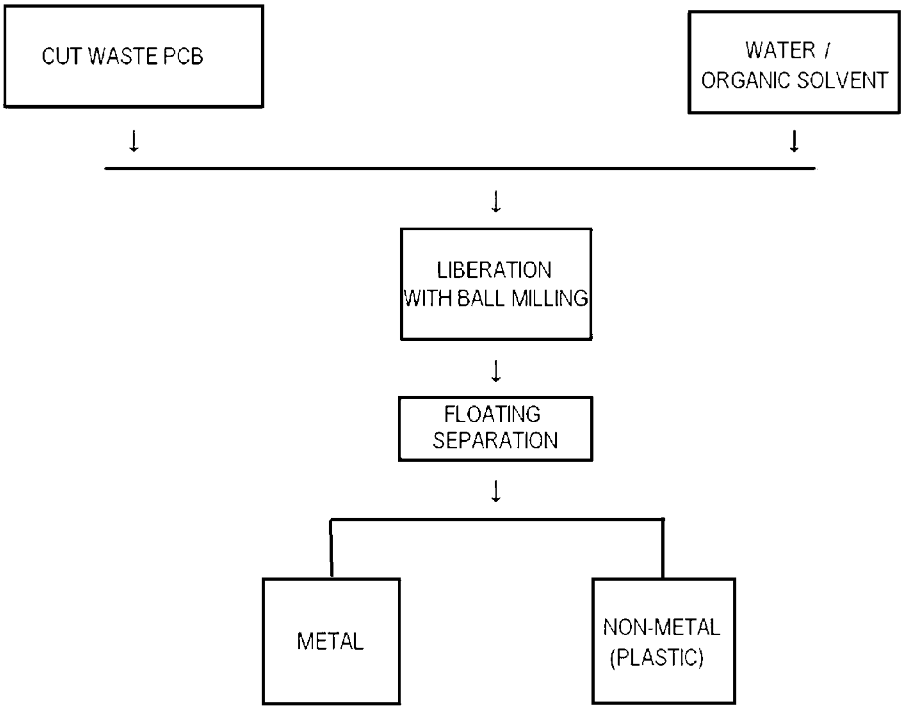
[Claim 5] The method of claim 4, wherein the ball milling is conducted at a revolution rate of 400 to 600 rpm for 30 to 120 minutes.

[Claim 6] The method of claim 4, wherein the balls used for the ball milling are metallic balls or ceramic balls having a particle size of 10 to 15 mm.

[Claim 7] The method of claim 6, wherein an amount of the injected balls is in the range of 5 to 10% of a volume of a grinding machine in the ball milling.

[Claim 8] The method of claim 1, wherein in the floating separation, 0.001 to 2% by weight of a floatation reagent is added to the pulp solution to float and recover the liberated metals.

[Fig. 1]


CUT WASTE PCB
WATER / ORGANIC SOLVENT
LIBERATION WITH BALL MILLING
FLOATING SEPARATION
METAL
NON-METAL (PLASTIC)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2013/008061

A. CLASSIFICATION OF SUBJECT MATTER

C22B 7/00(2006.01)i, B09B 3/00(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22B 7/00; C22B 34/20; B03B 5/20; B03B 5/28; C22B 15/00; B09B 3/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: ,PCBs , pulp, ball milling, floatation agent.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KR 10-2009-0106056A (주식회사 동방이엠티) 08 October 2009 See paragraph 10 - paragraph 27; claim 1 and figures 1 - 3.	1
Y		2-8
Y	KR 10-2003-0003974A (KOREA INSTITUTE OF GEOSCIENCE AND MINERAL RESOURCES) 1 4 January 2003 See page 4, line 31 - page 4, line 25; claim 1 and figure 1.	2-7
Y	JP 08-003655A (MITSUBISHI MATERIALS CORP) 09 January 1996 See paragraph [0007] - paragraph [0008]; claim 1 and figure 1.	8
A	KR 10-2011-0051368A (KIM, JIN SOO) 18 May 2011 See paragraph [0014] - paragraph [0035]; claims 1 - 2 and figures 1 - 2.	1-8

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
KR 10-2009-0106056 A	08/10/2009	None	
KR 10-2003-0003974 A	14/01/2003	None	
JP 08-003655A	09/01/1996	JP 02-792444 B2 JP 08-323321 A	03/09/1998 10/12/1996
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