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# FEASIBILITY ANALYSIS OF PRINT PASTES CO-DISPOSAL IN ANAEROBIC SLUDGE DIGESTERS

L. Bonomo, A. Rozzi and F. Malpei

*Department Hydraulic, Environmental and Survey Engineering, Politecnico di Milano, Piazza L. Da Vinci, 32 - 20133 Milano, Italy*

## ABSTRACT

Significant amounts of residual print pastes are produced by the industrial textile settlements of the Como area (Italy). Currently, these wastes are directly discharged in the sewer but it is unlikely that in the future this treatment through POTW will be further allowed. Therefore alternative ways of collection and disposal must be evaluated. The most suitable processes appear to be: drying, followed by incineration or landfilling, or anaerobic co-treatment with sewage sludge. The latter option was investigated at pilot scale and a technical feasibility analysis of the full-scale solution was carried out. Results are presented and discussed with reference to the impact that this solution would have on the performance of POTW and on the treatment costs of textile industrial wastewater. © 1997 IAWQ. Published by Elsevier Science Ltd

## KEYWORDS

Anaerobic digestion; drying; dyes; print pastes; textile wastewater; thickeners.

## INTRODUCTION

Textile industries which print fabrics produce significant amounts of residual print pastes, deriving from the preparation of the pastes and the cleaning of machinery. Currently in various countries, print pastes, though very thick, are diluted and disposed of together with other wastewater streams produced within the factories. In many cases, print pastes appreciably increase pollution of the industrial effluent, in terms of TKN, COD and colour, and, therefore, the cost that the factory must pay for treatment and disposal.

Wastewater load ratio between the industrial and the domestic effluents in the southern territory of the province of Como (Italy) is uncommon due to the high density of industrial textile settlements. Some 300 dyeing and printing factories are concentrated in an area of 80-90 $km^2$. Textile wastewaters are mixed with domestic effluents and treated in three main POTWs which receive altogether some 100,000 $m^3$/d. In Table 1 the main characteristics related to the three plants are reported. While the Como plant treats principally domestic wastewaters with a minor industrial component, the reverse is true for the other two plants.

Almost all these plants had operational problems and an inadequate effluents quality, taking into account the fact that the effluents were and still are discharged into very small streams (dilution ratio in the order of 1 or less) and that it is therefore necessary to comply with very stringent discharge standards. The main problems were related to COD loads considerably higher than the design loads, to the presence of dyes and surfactants in the effluent and to the only partial ammonification of the influent TKN, probably due to the large amount of azo dyes and to a partial inhibition of ammonification. In the Como plant influent, for example, the unbiodegradable TKN is approximately 15-17%, while in a domestic influent the unbiodegradable TKN is usually around 4-6% (IAWPRC, 1987).

Table 1. Characteristics of the POTW plants in the Como area

| Plant location | Flowrate ($m^3$/d) | Popul.Eq. (p.e.)* | CODin (mg/L) | TKNin (mg/L) | Textile organic load % |
|---|---|---|---|---|---|
| Como | 55,000 | 400,000 | 700-900 | 50-60 | 30 |
| Bulgarograsso | 20,000 | 137,000 | 650-850 | 45-55 | 80 |
| FinoMornasco | 24,000 | 131,000 | 500-700 | 45-50 | 75 |

(*)population equivalent calculated assuming 110 g COD/d per person

Several measures were taken in the last few years in order to improve the operating conditions and the effluent quality of these plants: to reduce the daily organic overload peak, the upstream textile mills have been requested in many cases to install equalisation tanks and discharge their effluents over seven days per week; in the Bulgarograsso plant a post-treatment based on sand filtration and ozonation was built in order to reduce the colour and the surfactants concentration of the effluent; the Como plant was revamped by adding powdered activated carbon to the nitrification and a chemical phosphorus post-precipitation followed by sand filtration.

In spite of these measures, any reduction of the pollutant load entering the POTWs would still be beneficial for the operation of the plant and the quality of the effluent. A relatively simple operation in that direction would be to prevent the discharge of print pastes into the sewer by the textile mills.

## THE PRINT PASTES

Print pastes are a very important component in the textiles printing process. As they make a waste which is somewhat unknown waste, they are described in some detail in the following. The main ingredients of print pastes are: thickeners, dyes, urea and other chemicals. Their composition is: 70-90% water; 1-4% thickeners; 0-14% urea; 3% dyes and 0-1% various chemicals (i.e. surfactants, solvents, chelating agents). COD and nitrogen concentrations are of the order of 40-250 g COD/kg and 20-30 g TKN/kg respectively. On average, their polluting load is assumed to be equal to 100 g COD/kg and 20 g TKN/kg.

Thickeners make fabric printing possible by preventing uncontrolled diffusion of the dye during its transfer from the frame pressed on the fabric. Natural or modified products (by carboxylation, hydroxyethylation and esterification), made of polysaccharides extracted from carob seeds, arabic gum and seaweeds are mainly used. Synthetic thickeners, made of long chain polymers derived from vinylic compounds, are also available.

Urea is added because of its hydrotropic and solvent properties, as it improves solubility of dyes which are scarcely water-soluble and fixes them on the fabric. It is mainly used for cotton and viscose and occasionally silk. Although printing installations which do not require urea are being developed and tested, in the Como area this method is still extensively used.

Several other chemicals are added to the printing pastes: hygroscopic products and solvents (mainly alcohols), antifoaming agents, sequestering and bonding agents.

Each print paste formula includes several chemicals belonging to the above classes. The actual composition of each recipe is very difficult to determine because in most cases the products (which are already mixtures of several ingredients) are identified only by a commercial brand name, and because the reluctance of the mill technicians to disclose the preparation details of the paste recipes. From the above considerations, the problems related to the chemical analysis of print pastes and to the related biological and physico-chemical treatment processes may be grasped more easily.

Print pastes are directly prepared at the factory when required. Initially the different thickeners are mixed until an homogeneous paste is obtained. The dye is also reduced to a paste which is mixed with the thickeners (plus urea and reducing agents if required) and diluted to reach the required colour shade. In order to print 100 $m^2$ of fabric, 25-40 kg of product are necessary.

As a result of the printing process, which is not described, appreciable amounts of residual paste are left on the frames and on the machinery. In most mills they prefer to produce more paste than required for precautional reasons, as it is almost impossible to produce two batches of the same shade. This excess product is normally left unused and has to be disposed, unless it is used to make much darker pastes. Altogether, 0.5-1 kg of product must be wasted per 100 $m^2$ of printed fabric. In the Como area this corresponds to some 10,000 to 20,000 kg of wasted print pastes to be disposed of daily.

## TREATMENT AND DISPOSAL PROCESSES

Currently, printing pastes are directly discharged into the sewer both in Italy and in some other countries (Buckley, 1995) while in Austria, Switzerland and Germany this procedure has already been forbidden. It is likely that, in the future, dilution of these wastes and subsequent treatment in POTWs will not be further allowed in Italy and therefore they will have to be collected and disposed of in an alternative way. The most suitable processes for print pastes disposal appear to be: drying, followed by incineration or landfilling, or anaerobic co-treatment with sewage sludge.

Direct incineration of separately collected print pastes is already carried out in Germanic countries, although it is quite expensive (cost of the order of 0.5 ECU/kg) because of the high water content and the low calorific value of these wastes. Moreover, problems related to emissions of nitrogen compounds in flue gases should be carefully considered. No direct experience of this process is available in Italy.

For the purpose to reduce transportation costs to final treatment or disposal sites, drying has been tested in a turbodrier (VOMM, Milano) at the Bulgarograsso plant. This full scale plant can process up to 1 ton/h of material and operates with the gas phase in closed circuit. Results related to preliminary tests (CIDA, 1996) seem to be satisfactory, although the peculiar rheological properties of these printing products, which contain gelatinous components, require a careful setting-up of the operating conditions. It has been found that a fraction of other material must be added (e.g. some 50% dried activated sludge on a wet mass basis). Otherwise dried print pastes become pitchy and difficult to extract from the cyclone after cooling. Humidity of print pastes is reduced from 84 to 5% while TKN increases from 22 to 118 g/kg (referred to the total weight). More than 90% of the original TKN in the pastes is recovered in the dried product. Ammonia transferred to the gas phase must be scrubbed and disposed of. Transfer of $NH_3$ to the biological wastewater treatment process and oxidation to nitrate is a feasible option.

Anaerobic treatment has been considered as a possible pre-treatment of print pastes notwithstanding a major disadvantage of this type of process, i.e. that it does not reduce the nitrogen contents of the waste. Although no direct information has been found in the literature on anaerobic digestion of print pastes as such, data are available related to most of their components. In general, thickeners are made of biodegradable products (the polysaccharide fraction), although some of them such as agar agar require specific bacterial strains, and consequently their anaerobic treatment might be proposed. An extensive bibliography is available on the anaerobic digestion of dyestuffs. Even though no general conclusion can be drawn due to the very large number of available molecules, one can assert that:

- a co-substrate seems to be necessary in most cases to promote the anaerobic degradation of dyes and related colour abatement;

- in general, anaerobic treatment leads to the breaking of the chromophore groups and not to the complete mineralization of the molecule (Brown and Laboureur, 1986);

- a higher removal is observed with dyes containing carboxylic radicals instead of sulphonic radicals (Mechsner and Wuhrmann, 1982);

- a fraction of the dyes seems to be removed by adsorption phenomena on the surface of the bacteria biomass (Shaul *et al.*, 1991). This phenomenon holds both for anaerobic and aerobic micro-organisms;

- no biodegradation of dyes is obtained in aerobic conditions, with an heterogeneous biomass (Shaul *et al.*, 1991);

- nitrogen removal by anaerobic degradation process is negligible. Nevertheless, it converts most of the TKN to ammonia which is the most convenient nitrogen species to remove by either biological or physicochemical downstream processes;

- intermediate products derived from the anaerobic treatment are much easier to degrade aerobically than the original molecules, In other words, a reductive pre-treatment effectively breaks those bonds which are difficult to attack by aerobic biological oxidation and therefore a combined anaerobic/aerobic treatment is more effective to degrade dyestuffs than either biological process.

In conclusion, anaerobic digestion of the residual print pastes as a pre-treatment would have several potential advantages: removal of an appreciable fraction of COD, colour reduction and conversion of the TKN to ammonia. $NH_3$ could be removed from the supernatant, which volume is relatively small, either by physicochemical stripping processes or by biological nitrification/denitrification.

Taking into account the above considerations, co-digestion of print pastes mixed with primary sludge in conventional anaerobic digesters in POTWs has been considered to be a possible interesting pre-treatment option for print pastes and it was therefore investigated at laboratory scale.

Table 2. Operating conditions of the laboratory co-digestion reactors (S: primary sludge; P1: Print paste with Turquoise Cibacron dye; P2: Print paste with Marine P dye; Pmix: mixture of waste print pastes of undetermined composition from several factories)

| | Feed % | COD load (g/L/d) | COD of paste ‡ |
|---|---|---|---|
| R1 | 95 S + 5 P1† → 97.5 S + 4 P1¥ | 2.112 | 4†- 2¥ |
| R2 | 95 S + 5 P2 | 2.462 | 18 |
| R3 | 95 S + 5 Pmix | 2.291 | 12 |
| R4 | 100 S | 2.125 | 0 |

† from day 0 to 60th, ¥ from day 74th to 140th
‡ as percentage of total influent COD

## ANAEROBIC TREATMENT OF PRINT PASTES AND SLUDGE

Anaerobic co-digestion of primary sludge and several kind of pastes was tested in four 3.5 litres volume completely stirred tank reactors operating at 35°C and fed once per day (fill and draw mode; HRT = SRT = 16 d). Primary sludge was used as cosubstrate, instead of a mixture of surplus biosolids, because the POTWs in the Como area include nitrification and denitrification phases. Their wasted secondary sludge is already almost stabilised due to the high sludge residence time and therefore it is not suitable for anaerobic digestion. Three digesters were fed on a mixture of pastes plus raw sludge while the fourth reactor was fed on sludge only and used as blank to detect possible inhibition phenomena in the digestion which could depend on sludge composition (e.g. toxicity due to absorbed halogenated hydrocarbons). On a weight basis, the mass of print pastes added to the sludge was in the range 2-5%. The reactors were inoculated with 3,000 ml of digested sludge (VSS = 11,42 g/l) from a POTW fed on domestic + industrial effluents (including textile wastewaters). Analyses were carried out according to standard methods (Standard Methods, 1995). Single pastes containing only one dye or a mixture of different pastes were tested, according to the conditions reported in Table 2.

After a first period lasting 50 days, i.e. more than 3 SRT = 3 HRT, acclimation was not completed as may be observed from Fig. 1, related to the concentration of volatile fatty acids. Indeed the TVA continued to increase in the three reactors R1, R2 and R3. Inhibition could tentatively be related both to ammonia and to dyes. In order to identify the inhibiting factor, feed was terminated in all reactors on the 60th day and half of the content of reactor R1 was transferred to another empty reactor (R5). The two vessels were then filled with distilled water to restore the initial volume. Dye and sludge concentrations in the reactors were therefore halved with respect to the initial conditions in R1. The reactors were left unfed during five days, and the methane production in this period was around 0.1-0.2 l/d. After six days, dye Turquoise Cibacron was added in reactor R5, in order to restore the dye concentration present in R1 before dilution. Apart from the dye addition to R5, R1 and R5 were left unfed during the inhibition test. After some 10 d of batch operation, the methane production rate of R1 was 0.25 against 0.05 l/d in R5. This result showed that the dye had a strong inhibiting effect.

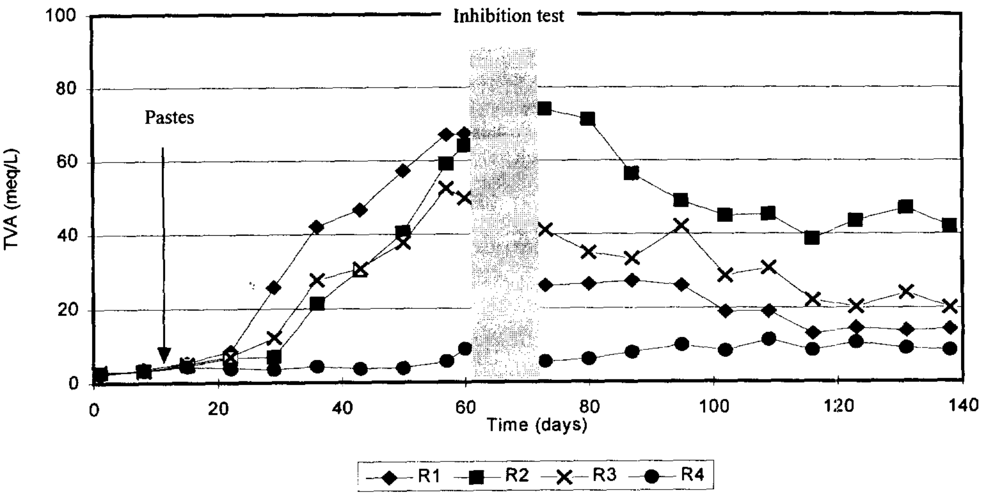


Figure 1. TVA concentration vs time during the print pastes/sludge co-digestion test.

After the inhibition test, operating conditions related to the reactors R2, R3 and R4 were brought back to the previous levels, while R1 was fed at a 4% dye load. During this period, acclimation was actually achieved as the plots related to the variables indicating "stressing conditions" such as TVA, pH and BA returned to more stable levels. It may be observed from Fig. 2, where methane production is plotted vs time, that during the second period the average productions for R1 and R3 were higher than the one related to R4 (control reactor).

The effluent COD at the end of the first phase was of the order of 10,500 mg COD/l for the three reactors fed on the paste-sludge mixture while it was 3,000 mg COD/l in the control reactor. At the end of the second phase, the effluent concentration was 3,600, 5,100, 3,700 and 2,100 mg COD/l in reactors R1, R2, R3, and

R4. The trends of concentration plots tended to decrease and level, which indicated that acclimation was successful.

Summarising this experiment, the anaerobic biomass needed more than three months to adapt to the print pastes (especially to dyestuffs) and provide acceptable performance. It must be noted that an adaptation time of the order of 3 months is not very long by anaerobic standards, especially if the feed contains toxic and/or xenobiotic compounds, At the end, COD removal and specific methane production of the reactors fed with pastes were comparable to the control reactor, particularly when an heterogeneous blend of different pastes (such as would occur in a in real scale application) was tested. Due to the high concentration of dissolved organics, COD concentration in the supernatant was appreciably higher than in the control reactor. The fraction of volatile acids in the supernatant was quite high too. The worst results were obtained for reactor R2 which was fed for the whole period with 5% paste containing one dyestuff only.

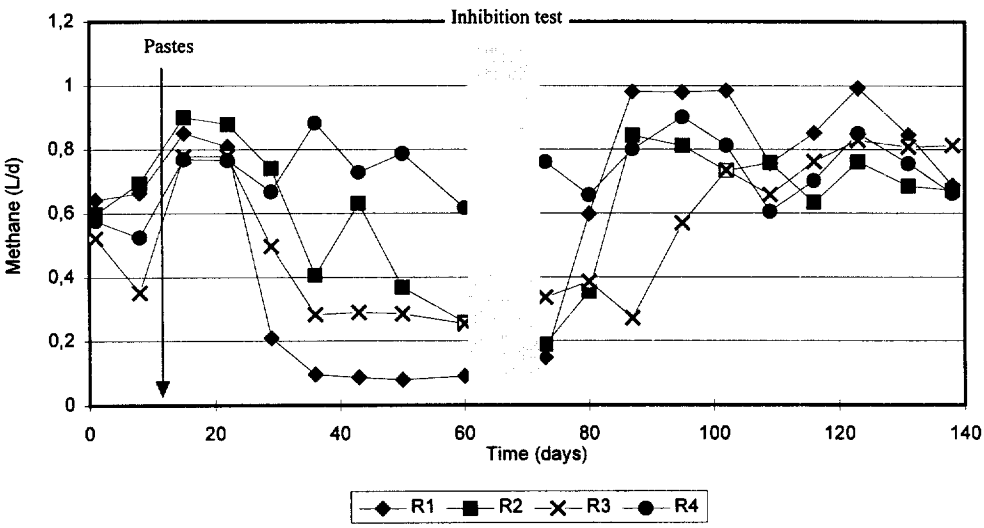


Figure 2. Methane production vs time during the print pastes/sludge co-digestion test.

The TKN of printing pastes, as might be expected theoretically, was almost completely recovered in the digested mixture. However, the ammonia content increased after the anaerobic digestion from 35% of raw print pastes TKN to over 60%. This value was calculated by subtracting the contribution of TKN hydrolysis due to the sludge in the control digester. Conversion of TKN to $NH_3$, which is typical of the anaerobic treatment, would be beneficial for the POTW because some organic components of print pastes are not easily degraded to release ammonia in aerobic conditions. Indeed, if the nitrogen load is mainly composed of organic nitrogen, nitrification in activated sludge plants can be limited by insufficient ammonification of TKN in the influent. Moreover, a specific ammonia removal treatment applied to the supernatant, which would remove also the ammonia hydrolysed during the anaerobic digestion of sludge, might be suggested to appreciably abate the nitrogen load to the aerobic plant.

A significant colour abatement was observed after the anaerobic treatment, on the basis of absorbance analysis in the visible spectrum (absorbance reduction from 1 to 0.1). It can be assumed that this removal of colouring materials is partly due to adsorption to the sludge matrix and partly to the anaerobic degradation of the chromophores of the dye molecules.

## TECHNICAL ANALYSIS OF CO-DIGESTION OF PASTES

Currently, none of the Como region POTWs fed on mixed domestic/textile effluents comprises anaerobic stabilisation of the waste sludge. The Como POTW, which is at present located in the city centre, should be transferred and completely rebuilt at a location outside the city. By this action, the final effluent will be discharged in surface streams which are a more suitable recipient body than the present one, the lake.

As the Como treatment plant has just recently been revamped, the complete transfer of the POTW will be carried out over a considerable length of time and a 15,000 $m^3$/d section will be built first in the near future. This section, mainly fed on domestic sewage, could be given an anaerobic digester. An appreciable fraction of waste print pastes, of the order of 4-5 tons wet weight, could be pre-treated in this digester.

The calculations for the co-digestion analysis are related to this 15,000 $m^3$/d case study. Assuming a primary sludge production of the order of 200 mg TSS per litre of raw wastewater, the overall production of primary sludge would be 3,000 kg TSS/d (approximately 100 $m^3$/d flow rate). Data related to the above laboratory co-digestion experiment correspond to the sludge/paste ratio in the planned first section of the new Como plant. The aim of the analysis was to evaluate the benefits in terms of loads reduction to the treatment plants in the case of separate collection and co-digestion of print paste. Therefore, it was necessary to evaluate the fractions of print pastes COD and TKN that would be transferred to the supernantant and, therefore, back to the POTW and to compare them with the total loads referred to the paste that actually arrives at the POTW diluted in the influent.

To evaluate these fractions, the following relation was adopted:

$$SUR, Pi = Qsur \cdot (Xsur, Ri - Xsur, R4)$$

where:

SUR, Pi: COD or TKN load referred to the paste Pi that would be transferred back to the plant with the supernatant;
Qsur: supernatant flow;
Xsur, Ri: COD or TKN concentration measured in the supernatant of the reactor containing the paste Pi;
Xsur, R4: COD or TKN concentration measured in the supernatant of the reactor R4 fed with primary sludge only (= 2,100 mg COD/l; 810 mg N/l).

In Table 3 the results of the balance for the paste Pmix, similar to the heterogeneous blend of waste pastes that would be fed to the digestor in case of a real-scale operation are reported.

Table 3. Evaluation of the percentage of the COD and TKN load referred to print paste that would be sent back to the plant with the supernatant, in case of co-disposal.

| Paste content ¥ | Amount of paste co-disposable † | Daily load associated to the paste | Xsur,R3 | SUR,Pmix ‡ | Ratio SUR,Pmix to load of paste |
|---|---|---|---|---|---|
| | | Mass balance on a COD basis | | | |
| gCOD/kg | (kg/d) | gCOD/d | (gCOD/$m^3$) | gCOD/d | |
| 113 | 5,000 | 57,000 | 3,700 | 140,800 | 0.25 |
| | | Mass balance on a TKN basis | | | |
| gN/kg | kg/d | gN/d | (gN/ $m^3$) | gN/d | |
| 11.4 | 5,000 | 57,000 | 1,200 | 53,680 | 0,94 |

¥ as concentration in the paste, on a wet basis
† on the basis of the same ratio paste/primary sludge adopted in reactor R3
‡ in the hypothesis that Qsur is equal to 88 $m^3$/d, being the digested sludge dewaterd to a 25% TSS content prior to the final disposal

As may be observed in Table 3, only 25% of the organic load referred to print pastes would be sent back to the POTW. Moreover, a substantial fraction of soluble COD in the liquid consists of volatile acids which can be used for downstream denitrification. As could be expected, almost all TKN referred to the pastes would be sent back to the plant. A specific treatment for ammonia removal on the supernatant flow, however, could be considered to reduce the load.

Recent results for full scale plants in Northern Europe (Thorndahl, 1992) indicate that stripping from digester supernatant might be an interesting treatment option for ammonia removal. But according to Siegrist (1996) the economics of this physico-chemical process are not very appealing because of the high amount of alkali to be added to the strongly buffered supernatant and the acid needed to absorb the ammonia; the total cost is of the order of 12 ECU/kg N. As an alternative option, nitrification-denitrification of ammonia nitrogen might be investigated. Indeed, according to Siegrist, for domestic wastewater treatment plants this process is probably the most economical, as nitrogen removal cost should be of the order of 4 ECU/kg N (calculations referred to a 100,000 inhabitants Swiss plant). Another reasonable possibility, still to be verified, would be to denitrify the supernatant with a reduced flow of recycled mixed liquor before entering the main pre-denitrification section of the POTW. This solution would enhance the removal of refractory compounds from the supernatant during the denitrification phase carried out at high concentration, prior to the dilution with the main stream of recycled activated sludge and would anyhow improve the overall removal because there would be two reactors in series instead of one only.

## CONCLUSIONS

The anaerobic digestion of small amounts of print pastes together with primary sludge may be a viable treatment and disposal option, to reduce the organic load of POTWs treating significant amounts of textile effluents, or in situations where the dilution and disposal of pastes with the industrial effluents is not permitted. At laboratory scale, the methane production in the co-digestors was similar or higher than the methane production of the control reactor fed with primary sludge only. Other beneficial aspects of this treatment are the partial reduction in the colour caused by the pastes, due to the breakage of the dyes chromofore in an anaerobic environment, and the improved ammonification of the TKN of print pastes, which may enhance the biological removal of TKN in the treatment plant.

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